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ELEMENTARY

CHEMISTRY,

THEORETICAL AND PRACTICAL.

BY

GEORGE FOWNES, PH.D.

CHEMICAL LECTURER IN THE MIDDLESEX HOSPITAL MEDICAL SCHOOL,
AND TO THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

EDITED, WITH ADDITIONS,

BY

ROBERT BRIDGES, M.D.,

PROFESSOR OF CHEMISTRY IN THE PHILADELPHIA COLLEGE OF PHARMACY, ETC. ETC.

A NEW EDITION.

WITH NUMEROUS ILLUSTRATIONS.

PHILADELPHIA:
LEA AND BLANCHARD.
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PREFACE

TO THE

AMERICAN EDITION.

THE Manual of Chemistry, now offered to the American student, will, it is hoped, supply a desideratum, by affording a work sufficiently full and complete on the elements of the science, without omitting any necessary information, or extending into too great minutiæ of detail. Written in a clear and succinct style, and aided by numerous wood-cuts representing the more simple modes of chemical manipulation, together with the facilities for comprehensive explanation afforded by the use of diagrams, it will be found to present the science in a form in which its acquisition will be much facilitated.

The original work having been full and complete up to the date of its publication, the task of the American editor has been to add any important matter which may have since appeared, and to correct such typographical errors as may have escaped the author's notice. The additional matter has been thrown into the form of notes—or where its publication has been subsequent to the printing of the subjects to which it properly refers, been placed in the Appendix, and in every instance distinguished by the editor's initials.

July, 1845.

THE approbation with which the Manual of Chemistry has been received by American teachers and students, has rendered a new edition necessary at this early day. The Editor has endeavored to respond to this approbation by such emendations and additions as are calculated to retain the advanced position which the original work has justly attained and to maintain it on an equality with the constant advance of chemical science.

June, 1847.

PREFACE.

THE design of the present volume is to offer to the student commencing the subject of Chemistry, in a compact and inexpensive, but, it is hoped, not unintelligible form, an outline of the general principles of that science, and a history of the more important among the very numerous bodies which Chemical investigations have made known to us. The work has no pretensions to be considered a complete treatise on the subject, but is intended to serve as an introduction to the larger and more comprehensive works in our own language and in those of the Continent.

It has been my aim throughout to render the book as practical as possible, by detailing at as great length as the general plan permitted, many of the working processes of the scientific laboratory, and by exhibiting, by the aid of numerous wood-engravings, the most useful forms of apparatus, with their adjustments and methods of use.

As one principal object was the production of a convenient and useful class-book for pupils attending my own lectures, I have been induced, although not without some misgivings, to adopt in the book the plan of arrangement followed in the lectures themselves, and to describe the non-metallic elements and some of their most important compounds before discussing the subject of the general philosophy of Chemical science, and even before describing the principle of the equivalent quantities, or explaining the use of the written symbolical language now universal among chemists. For the benefit of those to whom these matters are already familiar, and to render the history of the compound bodies described in the earlier part of the work more complete, I have added in foot-notes the view adopted of their Chemical constitution, expressed in symbols.

I have devoted as much space as could possibly be afforded to the very

important subject of Organic Chemistry; and it will, I believe, be found that there are but few substances of any general interest which have been altogether omitted. It may be pardoned, perhaps, if I venture to express the pain and regret I have felt during the composition of this portion of the work, from being compelled by the limited space allowed me, to treat a most interesting subject in a manner so brief and unsatisfactory.

GEO. FOWNES.

MIDDLESEX HOSPITAL,
Sep. 20, 1844.

TABLE OF CONTENTS.

PART I.

PHYSICS.

PAGE

OF DENSITY AND SPECIFIC GRAVITY.

Methods of determining the specific gravities of fluids and solids . 16
Construction and application of the hydrometer . . . 22

OF THE PHYSICAL CONSTITUTION OF THE ATMOSPHERE, AND OF GASES IN GENERAL.

Elasticity of gases.—Construction and use of the air-pump . 23
Weight and pressure of the air.—Barometer . . . 26
Law of Mariotte; relations of density and elastic force; correction of volumes of gases for pressure 27

HEAT.

Expansion.—Thermometers 30
Different rates of expansion among metals; compensation pendulum 33
Daniell's pyrometer 34
Expansion of liquids and gases.—Ventilation.—Movements of the atmosphere 35
Conduction of heat 40
Change of state.—Latent heat 41
Ebullition; steam 42
Distillation 45
Evaporation at low temperatures 47
Vapor of the atmosphere; hygrometry 48
Liquefaction of permanent gases 50
Production of cold by evaporation 52
Capacity for heat.—Specific heat 53
Sources of heat 55

PAGE

LIGHT.

Reflection, refraction, and polarization of light 56
Chemical rays 61
Radiation, reflexion, and absorption of heat 64
Transmission of heat 67

MAGNETISM.

Magnetic polarity; natural and artificial magnets 71
Terrestrial magnetism 73

ELECTRICITY.

Electrical excitation; machines 75
Principle of induction; accumulation of electricity . . 78
Voltaic electricity 80
Thermo-electricity.—Animal electricity 82
Electro-magnetism; magneto-electricity 82

PART II.

CHEMISTRY OF THE NON-METALLIC ELEMENTS.

Oxygen 88
Hydrogen; water; peroxide of hydrogen 93
Nitrogen; atmospheric air; compounds of nitrogen and oxygen . 102
Carbon; carbonic oxide; carbonic acid 108
Sulphur; compounds of sulphur and oxygen 112
Selenium 117
Phosphorus; compounds of phosphorus and oxygen . . . 117
Chlorine; hydrochloric acid.—Compounds of chlorine and oxygen . 120
Iodine 126
Bromine 128
Fluorine 128
Silicon 129
Boron 131

COMPOUNDS FORMED BY THE UNION OF THE NON-METALLIC ELEMENTS AMONG THEMSELVES.

Compounds of carbon and hydrogen.—Light carburetted hydrogen; olefiant gas; coal and oil-gases.—Combustion, and the structure of flame 132

PAGE

Nitrogen and hydrogen; ammonia 140
Sulphur, selenium and phosphorus, with hydrogen . . . 142
Chlorine, with sulphur and phosphorus 146
Other compounds 146

ON THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY.

Laws of combination by weight and volume . . . 148
Chemical symbols 155
The atomic theory 157
Chemical affinity 158
Electro-chemical decomposition; chemistry of the Voltaic pile . 161

PART III.

CHEMISTRY OF THE METALS.

General properties of the metals 170
Crystallography 177
Isomorphism 184
Theory of the constitution of salts 187
Potassium 190
Sodium 197
Ammonium 204
Lithium 207
Barium 208
Strontium 210
Calcium 210
Magnesium 215
Aluminium 218
Glucinum 220
Yttrium.—Zirconium.—Thorinum 221
Manufacture of glass, porcelain, and earthenware . . . 221
Manganese 225
Iron 228
Nickel 235
Cobalt 237
Zinc 238
Cadmium 239
Bismuth 240

PAGE

Uranium 241
Copper 242
Lead 244
Cerium and Lantanum 247
Chromium 248
Tin 250
Tungsten.—Molybdenum 252
Vanadium 253
Columbium (Tantalum).—Titanium 254
Antimony 255
Tellurium 257
Arsenic 258
Silver 263
Gold 266
Mercury 268
Platinum 273
Palladium 275
Rhodium 276
Iridium 277
Osmium 279

PART IV.

ORGANIC CHEMISTRY.

INTRODUCTION 280
THE ULTIMATE ANALYSIS OF ORGANIC BODIES . . . 283
EMPIRICAL AND RATIONAL FORMULÆ 292

DETERMINATION OF THE DENSITY OF THE VAPORS OF VOLATILE LIQUIDS 293

SACCHARINE AND AMYLACEOUS SUBSTANCES, AND THE PRODUCTS OF THEIR ALTERATION 295

Cane and grape-sugars; sugar of the eucalyptus; sugar from ergot of rye; sugar of diabetes insipidus; liquorice-sugar; milk-sugar; mannite 295
Starch; dextrine; starch from Iceland moss; inuline; gum; pectine; lignine 299

	PAGE
Oxalic acid	303
Saccharic acid; xyloidine; mucic acid	305
Suberic; Mellitic, rhodizonic, and croconic acids	306
Fermentation of sugar.—Alcohol	307
Lactic acid	310
Ether, and ethyle-compounds	312
Sulphovinic, phosphovinic, and oxalovinic acids	316
Heavy oil of wine	319
Olefiant gas; Dutch liquid; chlorides of carbon	320
Ethionic and isethionic acids	323
Chloral, &c.	324
Mercaptan; xanthic acid	325
Aldehyde; aldehydic acid; acetal	326
Acetic acid	328
Chloracetic acid	331
Acetone	332
Kakodyle	333

SUBSTANCES MORE OR LESS ALLIED TO ALCOHOL.

Wood-spirit; methyle-compounds	337
Sulphomethylic acid	339
Formic acid	340
Chloroform; formomethylal; methyl-mercaptan	341
Potato-oil and its derivatives	342
Sulphamilic acid	343
Valerianic acid; chlorovalerisic and chlorovalerosic acids	344
Fusel-oil from grain-spirit	345
Bitter almond oil and its products; benzoyle compounds	345
Benzoic acid; sulphobenzoic acid; benzone and benzine	346
Sulphobenzide and hyposulphobenzic acid; nitrobenzide	348
Mandelic acid; hydrobenzamide	349
Benzoine; benzile; benzilic acid; benzimide	350
Hippuric acid	350
Salicine; salicyle and its compounds	351
Chlorosamide.—Phloridzine	353
Cinnamyle and its compounds; cinnamic acid; chloro-cinnose	353

VEGETABLE ACIDS.

Tartaric acid	356
Racemic acid	358
Citric acid	359
Aconitic or equisetic acid	359

PAGE

Malic acid 360
Fumaric and maleic acids 360
Tannic and gallic acids 361

AZOTIZED ORGANIC PRINCIPLES OF SIMPLE CONSTITUTION

Cyanogen; paracyanogen; hydrocyanic acid . . . 365
Amygdaline; amygdalinic acid 367
Cyanides 369
Cyanic, cyanuric, and fulminic acids 371
Chlorides, &c. of cyanogen 374
Ferro, and ferridcyanogen, and their compounds; Prussian blue . 375
Cobaltocyanogen 378
Sulphocyanogen, and its compounds; melam; melamine; ammeline; ammelide 378
Urea, and uric acid 380
Allantoin; alloxan; alloxanic acid; mesoxalic acid; mykomelinic acid; parabanic acid; oxaluric acid; thionuric acid; uramile; alloxantine; murexide; murexan 382
Xanthic and cystic oxides 386

THE VEGETO-ALKALIS, AND ALLIED BODIES.

Morphia, and its salts 388
Codeine; thebaine; pseudomorphine; narceine; meconine . 389
Meconic acid 389
Cinchonia and quina; aricine 390
Kinic acid 391
Strychnia and brucia; veratria; conicine; nicotine . . 391
Hyoscyamine; daturine; atropine; solanine; delphinine; emetine; curarine 392
Gentianine; populine; daphnine; hesperidine; elaterine; piperine; antiarine; picrotoxine; asparagine; caffeine, or theine; theobromine 392

ORGANIC COLORING PRINCIPLES.

Indigo; white indigo; sulphindigotic acid 394
Anilic and picric acids 395
Isatine; chrysanilic and anthranilic acids; chrysammic and chrysolepic acids 396
Litmus—lecanorine; orcine; orceine 396
Cochineal, madder, dye-woods 397

OILS AND FATS.

Fixed oils; margarine, stearine, and oleine . . . 398

PAGE

Saponification, and its products; glycerine . . . 399
Palm and cocoa-oils.—Elaidine and elaidic acid . . . 401
Suberic, succinic, and sebacic acids 402
Butyrine: butyric acid 402
Wax; spermaceti; cholesterine; cantharidine . . . 403
Volatile oils.—Oils of turpentine and lemons.—Oils of mustard-seed, horseradish, assafœtida, and hops 403
Resins and Balsams 405

COMPONENTS OF THE ANIMAL BODY.

Albumen, fibrine, and caseine; proteine 407
Gelatine and chondrine 411
Composition of the blood; respiration; animal heat . . 413
Chyle; lymph; mucus; pus 417
Milk; bile; urine; urinary calculi 418
Nervous substance; membranous tissue; bones . . . 425
The function of nutrition in the vegetable and animal kingdoms . 427

PRODUCTS OF THE DESTRUCTIVE DISTILLATION, AND SLOW PUTREFACTIVE CHANGE OF ORGANIC MATTER.

Substances obtained from tar.—Paraffine; eupione; picamar; kapnomor; cedriret; pittakal; kreosote; chrysen and pyren . 432
Coal-oil.—Kyanol and leukol.—Carbolic acid . . . 435
Naphthaline and paranaphthaline 436
Petroleum, naphtha, and other allied substances . . . 437

APPENDIX.

On the equivalent numbers—Hydrometer tables.—Table of the tension of the vapor of water at different temperatures.—Table of the proportion of real alcohol in spirits of different densities.—Table of weights and measures.—Analysis of the mineral waters of Germany 439

INDEX. 451

LIST OF ILLUSTRATIONS

BY WOOD CUTS.

Fig.		PAGE
1	Specific gravity bottle -	18
2	" " - -	19
3	" " - -	19
4	" " - -	19
5	" " beads -	21
6	Hydrometer - - -	22
7	Elasticity of gases -	23
8	Single air-pump - -	24
9	Double " - -	25
10	Improved " - -	25
11	" " - -	26
12	Barometer - - -	27
13	" - - -	28
14	" - - -	29
15	Expansion of solids -	30
16	" liquids -	30
17	" gases -	30
18	Differential thermometer -	32
19	" " -	32
20	Difference of expansion in metals - - -	33
21	Gridiron pendulum -	33
22	Mercury " - -	34
23	Compensation balance -	34
24	Daniell's pyrometer -	34
25	Expansion of liquids -	36
26	Atmospheric currents -	38
27	" " -	39
28	" " -	39
29	Boiling paradox - -	43
30	Steam-bath - - -	44
31	Steam-engine - - -	45
32	Distillation - - -	46
33	Liebig's condenser - -	46
34	Tension of vapor - -	47
35	" " - -	48
36	Wet-bulb hygrometer -	50
37	Condensation of gases -	50
38	Thilorier's apparatus -	51
39	Cold by evaporation -	52
40	Wollaston's Cryophorus -	52
41	Daniell's hydrometer -	53
42	Reflection of light - -	56
43	Refraction of light - -	57
44	" " - -	57
45	" " - -	58
46	Spectrum - - -	58
47	" - - - -	59
48	Polarization of light -	60
49	" " -	60
50	" " -	60
51	Reflection of heat - -	64
52	" " - -	65
53	Effects of electrical current on the magnetic needle	67
54	" " " -	67
55	Current produced by heat	68
56	Mellonis's instrument for measuring transmitted heat - - -	68
57	Magnetic polarity - -	72
58	" " - -	72
59	Electric repulsion - -	75
60	Electroscope - - -	75
61	Electric polarity - -	76
62	Electrical machine, cylinder	77
63	" " plate -	78
64	Leyden jar - - -	79
65	Electrophorus - -	79
66	Volta's pile - - -	80
67	Crown of cups - -	81
68	Cruikshank's trough -	81
69	Effect of electrical current on the magnetic needle	83
70	Astatic needle - -	83
71	Magnetism developed by the electrical current -	84
72	" " -	84
73	Electro-magnet - -	85
74	Apparatus for oxygen -	88
75	Hydro-pneumatic trough -	89
76	Transferring of gases -	90
77	Pepys' hydro-pneumatic apparatus - - -	90
78	Apparatus for hydrogen -	93
79	Levity of hydrogen -	94

Fig.		PAGE
80	Diffusion of gases	95
81	" "	95
82	Hemming's safety jet	96
83	Musical sound from hydrogen	97
84	Catalytic effect of platinum	98
85	Decomposition of water	98
86	Eudiometer of Cavendish	99
87	Analysis of water	99
88	Apparatus for nitrogen	102
89	Analysis of air	104
90	Ure's eudiometer	104
91	Preparation of protoxide of nitrogen	107
92	Crystalline forms of carbon	108
93	Preparation of carbonic acid	110
94	Mode of forming caoutchouc connecting tubes	110
95	Crystals of sulphur	112
96	" "	112
97	Preparation of phosphorus	118
98	" chlorine	120
99	" hydrochloric acid	122
100	Safety-tube	123
101	Fire under water	125
102	Preparation of phosphuretted hydrogen	127
103	" silicic acid	130
104	Blast furnace	136
105	Reverberatory furnace	136
106	Structure of flame	137
107	Mouth blow-pipe	137
108	Flame from blow pipe	138
109	Spirit-lamp	138
110	"	138
111	Use of illuminating gas for heat	138
112	Davy's safety-lamp	139
113	Hemming's safety-tube	140
114	Effect of metal on flame	140
115	Apparatus for sulphuretted hydrogen	142
116	Multiple proportions	158
117	Water in its usual state	163
118	" undergoing electrolysis	164
119	Voltameter	165
120	Galvanism without contact	166
121	Wollaston's voltaic battery	168
122	Daniell's constant "	168
123	Grove's " "	169
124	Electrotype "	169
125	Lead-tree	170
126	Wire-drawing	172
127	Wollaston's goniometer	178
128	Reflective "	178
129	" " principles of	179
130	Crystals, regular system	180
131	" square prismatic system	181
132	" right prismatic system	181
133	" oblique prismatic system	182
134	" double oblique prismatic system	182
135	" rhombohedral system	183
136	" passage of cube to octahedron	183
137	" " of octahedron to tetrahedron	184
138	Alkalimeter	200
139	Apparatus for determining the proportion of carbonic acid	201
140	Iron manufacture. Blast furnace	233
141	Subliming tube for arsenic	260
142	Marsh's apparatus	262
	Organic analysis:—	
143	Weighing tube	284
144	Tube of combustion	284
145	Apparatus complete	285
146	Chauffer	285
147	Water-tube	285
148	Carbonic acid bulbs	285
149	Apparatus arranged	286
150	Bulbs for liquids	287
151	Comparative determination of nitrogen	288
152	Pipette	288
153	Absolute estimation of nitrogen	289
154	Method of Will & Varrentrapp	291
155	Determination of the density of vapors	293
156	Starch granules magnified	300
157	Apparatus for preparation of ether	319
158	" of olefiant gas	321
159	" Dutch liquid	321
160	Catalysis	328
161	Preparation of kakodyle	335
162	" benzoic acid	346
163	" tannic acid	361
164	Blood globules magnified	414

A

MANUAL OF CHEMISTRY.

PART I.—PHYSICS.

OF DENSITY AND SPECIFIC GRAVITY.

It is of great importance in the outset to understand clearly what is meant by the terms *density* and *specific gravity*. By the *density of a body* we mean its *mass* or *quantity of matter*, compared with the mass or quantity of matter of an *equal volume* of some standard body, arbitrarily chosen. *Specific gravity* denotes the *weight* of a body, as compared with the weight of an equal bulk, or volume, of the standard body which is reckoned as unity.* In all cases of solids and liquids this standard of unity is pure water at the temperature of 60° Fahr. Anything else might have been chosen; there is nothing in water to render its adoption for the purpose mentioned indispensable; it is simply taken for the sake of convenience, being always at hand, and easily obtained in a state of perfect purity. The ordinary expression of specific weight, therefore, is a number expressing how many times the weight of an equal bulk of water is contained in the weight of the substance spoken of. If, for example, we say that concentrated oil of vitriol has a specific gravity equal to 1·85, or that perfectly pure alcohol has a density of ·794 at 60°, we mean that equal bulks of these two liquids and of distilled water possess weights in the proportion of the numbers 1·85, ·794, and 1; or 1850, 794, and 1000. It is necessary to be particular about the temperature, for, as will be hereafter shown, liquids are extremely expansible by heat; otherwise, a constant bulk of the same liquid will not retain a constant weight. It will be proper to begin with the description of the mode in which the specific gravity of liquids is determined; this is the simplest case, and the one which best illustrates the general principle.

In order to obtain at pleasure the specific gravity of any particular liquid compared with that of water, it is only requisite to weigh equal bulks at the standard temperature, and then divide the weight of the liquid by the weight of the water; the quotient will of course be greater or less than unity, as the liquid experimented on is heavier or lighter than water. Now, to weigh equal

* In other words, density means comparative *mass*, and specific gravity comparative *weight*. These expressions, although really relating to distinct things, are often used quite indifferently in chemical writings, and without practical inconvenience, since mass and weight are directly proportional to each other.

bulks of two fluids, the simplest and best method is clearly to weigh them in succession in the same vessel, taking care that it is equally full on both occasions; a condition very easy of fulfilment.

Fig. 1.

A thin glass bottle or flask, with a narrow neck, is procured, of the figure represented in the margin, and of such capacity as to contain, when filled to about half way up the neck, exactly 1000 grains of distilled water at 60°. Such a flask is easily procured from any one of the Italian artificers, to be found in every large town, who manufacture cheap thermometers for sale. A counterpoise of the exact weight of the empty bottle is made from a bit of brass, an old weight or something of the kind, and carefully adjusted by filing; an easy task. The bottle is then graduated, by introducing water at 60°, until it exactly balances the 1000-grain weight and counterpoise in the opposite scale; the height at which the water stands in the neck is marked by a scratch, and the instrument is complete for use; the liquid to be examined is brought to the temperature of 60°, and with it the bottle is filled up to the mark before mentioned; it is then weighed, the counterpoise being used as before, and the specific gravity directly ascertained.

A watery liquid in a narrow glass tube, always presents a curved surface from the molecular action of the glass, the concavity being upwards. It is better on this account in graduating the bottle, to make two scratches, as represented in the drawing, one at the top and the other at the bottom of the curve; this prevents any future mistake. The marks are easily made by a fine, sharp, three-square file, the hard point of which also, it may be observed, answers perfectly well for writing upon glass, in the absence of a proper diamond-pencil.

The specific gravity bottle above described differs from those commonly made for sale by the instrument-makers. These latter are constructed with a perforated stopper, so arranged that when the bottle is quite filled, the stopper put in its place, and the excess of liquid which flows through the hole, wiped from the outside, a constant measure is always had. There are inconveniences attending the use of the stopper which lead to a preference of the open bottle with merely a mark in the neck, even when very volatile liquids are experimented on.

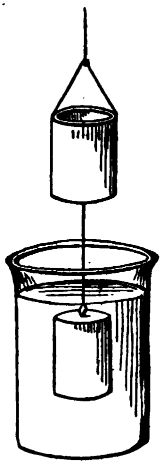
It will be quite obvious that the adoption of a flask holding exactly 1000 grains of water has no other object than to save the trouble of a very trifling calculation; any other quantity would answer just as well, and, in fact, the experimental chemist is often compelled to use a bottle of much smaller dimensions, from scarcity of the liquid to be examined. The shape is also in reality of little moment; any light phial with a narrow neck may be employed, not quite so conveniently perhaps, as a specific gravity bottle.

The determination of the specific gravity of a solid is also an operation of great facility, although the principle is not so obvious. As it would be impossible to put in practice a direct method like that indicated for liquids, recourse is had to another plan. The celebrated theorem of Archimedes affords a solution of the difficulty. The theorem may be thus expressed:—

When a solid is immersed in a fluid, it loses a portion of its weight; and this portion is equal to the weight of the fluid which it displaces; that is, to the weight of its own bulk of that fluid.

It is easy to give experimental proof of this very important proposition, as well as to establish it by reasoning. The drawing represents a little apparatus for the former purpose. This consists of a thin cylindrical vessel of brass, into the interior of which fits very accurately a solid cylinder of the same metal, thus exactly filling it. When the cylinder is suspended beneath the bucket, as seen in the sketch, the whole hung from the arm of a balance and counterpoised, and then the cylinder itself immersed in water, it will be found to have lost a certain weight; and that this loss is precisely equal to the weight of an equal bulk of water, may then be proved by filling the bucket to the brim, whereupon the equilibrium will be restored.

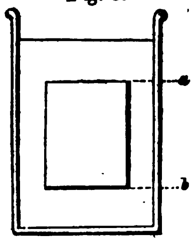
Fig. 2.



The consideration of the great hydrostatic law of fluid pressure easily proves the truth of the principle laid down. Let the reader figure to himself a vessel of water, having immersed in it a solid cylindrical or rectangular body, and so adjusted with respect to density that it shall float indifferently in any part beneath the surface.

Now the law of fluid pressure is to this effect:—The pressure exerted by a fluid upon the containing vessel, or upon anything plunged beneath its surface, depends, first, upon the density of that fluid, and, secondly, upon the perpendicular heights of the column. Moreover, owing to the peculiar physical constitution of fluids, this pressure is exerted equally in every direction, upwards, downwards, and laterally, with equal force.

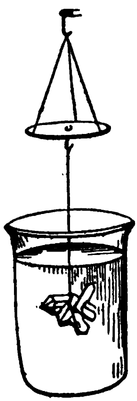
Fig. 3.



The floating body is in a state of equilibrium; therefore the pressure downwards caused by its gravitation must be exactly compensated by the upward transmitted pressure of the column of water *a b*.

But this pressure downwards is obviously equal to the weight of an equal quantity of water, since the body of necessity displaces its own bulk.—

Fig. 4.



Hence, the weight lost, or supported by the water, is the weight of a volume of water equal to that of the body immersed.

Whatever be the density of the substance, it will be buoyed up to this amount; in the case supposed, the buoyancy is equal to the whole weight of the body, which is thus, while in the water, reduced to nothing.

A little reflection will show that the same reasoning may be applied to a body of irregular form; besides, a solid of any figure may be divided by the imagination into a multitude of little perpendicular prisms, or cylinders, to each of which the argument may be applied. What is true of each individually, must necessarily be true of the whole together.

This is the fundamental principle; its application is made in the following manner:—Let it be required, for example, to know the specific gravity of a body of extremely irregular form, as a small group of rock-crystals: the first part of the operation consists in

determining its absolute weight, or, more correctly speaking, its weight in air; it is next suspended from the balance-pan by a fine silk thread, immersed completely in pure water at 60°, and again weighed. It now weighs less, the difference being the weight of the water it displaces, that is, of an equal bulk. This being known, nothing more is required than to find, by division, how many times the latter number is contained in the former; the quotient will be the density, water being taken = 1.

The quartz-crystals weigh in air	293·7 grains.
When immersed in water, they weigh	180·1
Difference, being the weight of an equal volume of water	113·6

$$\frac{293{\cdot}7}{113{\cdot}6} = 2{\cdot}58, \text{ the specific gravity required.}$$

The arbitrary rule is generally thus written: "Divide the weight in air by the loss of weight in water, and the quotient will be the specific gravity." In reality, it is not the weight in air which is required, but the weight the body would have in empty space: the error introduced is so trifling that it is usually neglected.

Sometimes the body to be examined is lighter than water, and floats. In this case, it is first weighed and afterwards attached to a piece of metal, heavy enough to sink it, and suspended from the balance. The whole is then exactly weighed, immersed in water, and again weighed. The difference between the two weighings gives the weight of a quantity of water equal in bulk to both together. The light substance is then detached, and the same operation of weighing in air, and again in water, repeated on the piece of metal. These data give the means of finding the density, as will be at once seen by the following example:—

Light substance (a piece of cork) weighs in air .	39·6 grains.
Attached to a piece of brass; the whole now weighs	519·6
Immersed in water, the system weighs	294·1
Weight of water equal in bulk to brass and cork .	225·5
Weight of brass in air	480·
Weight of brass in water	422·
Weight of equal bulk of water	58·
Bulk of water equal to cork and brass	225·5
Bulk of water equal to brass alone	58·
Bulk of water equal to cork alone	167·5

$$\frac{39{\cdot}6}{167{\cdot}5} = .236$$

In all such experiments it is necessary to pay attention to the temperature and purity of the water, and to remove with great care all adhering air bubbles; otherwise a false result will be obtained.

The substance to be examined may be in small fragments, or powder. Here the operation is very simple. A bottle holding a known weight of water is taken; the specific gravity bottle already described answers perfectly well. A convenient quantity of the substance is next carefully weighed out, and

introduced into the bottle, which is then filled up to the mark on the neck with distilled water. It is clear that the vessel now contains less water by a quantity equal to the bulk of the powder than if it were filled in the usual manner. It is, lastly, weighed. In the subjoined experiment emery powder was tried.

The bottle held, of water	1000 grains.
The substance introduced weighed . .	100
Weight of the whole, had no water been displaced .	1100
The observed weight is, however, only . .	1070
Hence, water displaced, equal in bulk to the powder	30

$$\frac{100}{30} = 3.333 \text{ specific gravity.}$$

There is yet another case which requires mention,—that, namely, in which the substance is dissolved or acted upon by water. This difficulty is easily conquered by substituting some other liquid of known density which experience shows is without action. Alcohol or oil of turpentine may generally be used when water is inadmissible. Suppose, for instance, the density of crystallized sugar is required, we proceed in the following way: The specific gravity of the oil of turpentine is first carefully determined: let it be ·87; the sugar is next weighed in the air, then suspended by a thread, and weighed in the oil; the difference is the weight of an equal bulk of the latter; a simple calculation gives the weight of a corresponding volume of water:

Weight of sugar in air	400 grains.
Weight of sugar in oil of turpentine . .	182·5
Weight of equal bulk of oil of turpentine . .	217·5

$$87 : 100 : : 217{\cdot}5 : 250,$$

the weight of an equal bulk of water; hence the density of the sugar,

$$\frac{400}{250} = 1{\cdot}6.$$

The theorem of Archimedes affords the key to the general doctrine of the equilibrium of floating bodies, of which an application is made in the common hydrometer,—an instrument for finding the densities of liquids in a very easy and expeditious manner.

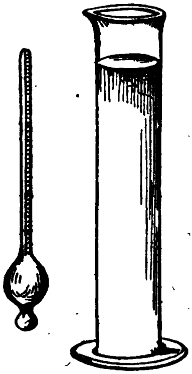
When a solid body is placed upon the surface of a fluid specifically heavier than itself, it sinks down until it displaces a quantity of fluid equal to its own weight, at which point it floats. Thus in the case of a substance floating in water, whose specific weight is one half that of the fluid, the position of equilibrium will involve the immersion of exactly one half the body, inasmuch as its whole weight is counterpoised by a quantity of water equal to half its volume. If the same body were put into a fluid of one half the density of water, if such could be found, then it would sink beneath the surface, and remain indifferently in any part. A floating body of known density may thus be used as an indicator of the specific gravity of a fluid. In this manner little glass beads of known densities are sometimes employed in the arts to ascer-

Fig. 5.

tain in a rude manner the specific gravity of liquids; the one that floats indifferently beneath the surface without either sinking or rising, has of course the same specific gravity as the liquid itself; this is pointed out by the number marked upon the bead.

The hydrometer in general use consists of a floating vessel of thin metal or glass, having a weight beneath to maintain it in an upright position, and a stem above bearing a divided scale. The use of the instrument is very simple. The liquid to be tried is put into a small narrow jar, and the instrument floated in it. It is obvious that the denser the liquid, the higher will the hydrometer float, because a small displacement of fluid will counterbalance its weight. For the same reason, in a liquid of less density, it sinks deeper. The hydrometer comes to rest almost immediately, and then the mark on the stem at the fluid-level may be read off.

Fig. 6.



Very extensive use is made of instruments of this kind in the arts; these sometimes bear different names, according to the kind of liquid for which they are intended; but the principle is the same in all. The graduation is very commonly arbitrary, two or three different scales being, unfortunately, used. These may be reduced by calculation, however, to the true numbers expressing the specific gravity.

A very convenient and useful instrument in the shape of a small hydrometer for taking the specific gravity of urine, has lately been put into the hands of the physician; it may be packed into a pocket-case, with a little jar and a thermometer, and is always ready for use.*

The determination of the specific gravity of gases and vapors of volatile liquids is a problem of very great practical importance to the chemist; the theory of the operation is as simple as when liquids themseles are concerned; but the processes are much more delicate, and involve, besides, certain corrections for differences of temperature and pressure, founded on principles yet to be discussed. It will be proper to defer the consideration of these matters for the present.

* These, and other instruments described or figured in the course of the work, may be had of Mr. Newmann, 122 Regent-street, upon the excellence of whose workmanship reliance may be safely placed.

OF THE PHYSICAL CONSTITUTION OF THE ATMOSPHERE, AND OF GASES IN GENERAL.

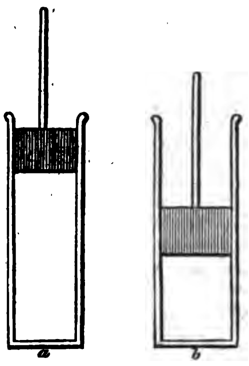
It requires some little abstraction of mind to realize completely the singular condition in which all things at the surface of the earth exist. We live at the bottom of an immense ocean of gaseous matter, which envelops everything, and presses upon everything with a force which appears at first sight perfectly incredible, but whose actual amount admits of easy proof.

Gravity being, so far as is known, common to all matter, it is natural to expect that gases, being material substances, should be acted upon by the earth's attraction, as well as solids and liquids. This is really the case, and the result is the weight or pressure of the atmosphere, which is nothing more than the effect of the attraction of the earth on the particles of air.

Before describing the leading phenomena of the atmospheric pressure, it is necessary to notice one very remarkable feature in the physical constitution of gases, upon which depends the principle of an extremely valuable instrument, the air-pump.

Gases are in the highest degree elastic; the volume or space which a gas occupies depends upon the pressure exerted upon it. Let the reader imagine a cylinder, *a*, closed at the bottom, in which moves a piston, air-tight, so that no air can escape between the piston and the cylinder. Suppose now the piston be pressed downwards with a certain force; the air beneath will be compressed into a smaller bulk, the amount of this compression depending on the force applied; if the power be sufficient, the bulk of the gas may be thus diminished to one hundredth part or less. When the pressure is removed, the elasticity or *tension*, as it is called, of the included air or gas, will immediately force up the piston until it arrives at its first position.

Fig. 7.



Again, take fig. *b*, and suppose the piston to stand about the middle of the cylinder, having air beneath in its usual state. If the piston be now drawn upwards, the air below will expand, so as to fill completely the increased space, and this to an apparently unlimited extent. A volume of air which under ordinary circumstances occupies the bulk of a cubic inch, might, by the removal of the pressure upon it, be made to expand to the capacity of a whole room, while a renewal of the former pressure would be attended by a shrinking down of the air to its former bulk. The smallest portion of gas introduced into a large exhausted vessel becomes at once diffused through the whole space, an equal quantity being present in every part; the vessel is *full*, although the gas is in a state of extreme tenuity. This power of expansion which gases possess may have, and probably has, in reality, a limit; but the limit is never reached in practice. We are quite safe in the assumption, that for all purposes of experiment, however refined, gases are perfectly elastic.

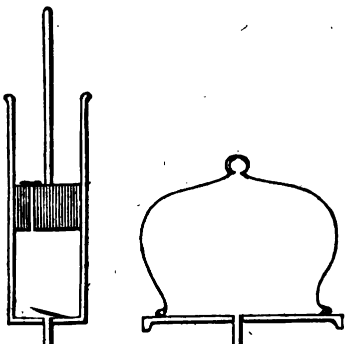
It is usual to assign a reason for this indefinite expansibility by ascribing

to the particles of material bodies, when in a gaseous state, a self-repulsive energy. The statement is commonly made somewhat in this manner: Matter is under the influence of two opposite forces, one of which tends to draw the particles together, the other to separate them; by the preponderance of one or other of these forces, we have the three states called solid, liquid, and gaseous. When the particles of matter are immovably bound together by the attractive force, a solid substance results; when the forces are nearly balanced, we have a liquid, the particles of which are free to move, but yet to a certain extent held together; and lastly, when the attractive power seems to be completely overcome by its antagonist, we have a gas or vapor.

Various names are applied to these forces, and various ideas entertained concerning them; the attractive forces bear the name of cohesion when they are exerted between particles of matter separated by a very small interval, and gravitation, when the distance is great. The repulsive principle is often thought to be identical with the principle of heat.

The ordinary air-pump, shown in section in fig. 8, consists essentially of a metal cylinder, in which moves a tightly fitting piston, by the aid of its rod. The bottom of the cylinder communicates with the vessel to be exhausted, and is furnished with a valve opening upwards. A similar valve, also opening upwards, is fitted to the piston; these valves are made with slips of oiled silk. When the piston is raised from the bottom of the cylinder, the space left beneath it must be void of air, since the piston-valve opens only in one

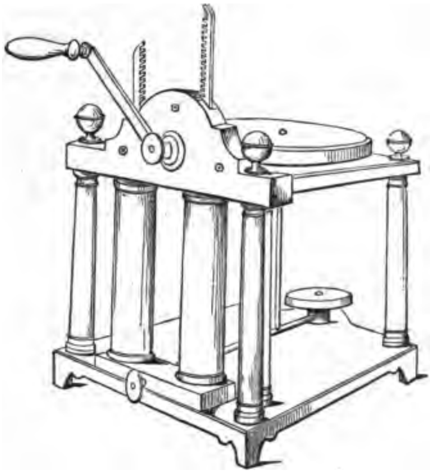
Fig. 8.



direction; the air within the receiver having on that side nothing to oppose its elastic power but the weight of the little valve, lifts the latter, and escapes into the cylinder. So soon as the piston begins to descend, the lower valve closes, by its own weight, or by the transmitted pressure from above, and communication with the receiver is cut off. As the descent of the piston continues, the air included within the cylinder becomes compressed, its elasticity is increased, and at length it forces open the upper valve, and escapes into the atmosphere. In this manner a cylinder full of air is at every stroke of the pump removed from the receiver; during the descent of the piston, the upper valve remains open, and the lower closed, and the reverse during the opposite movement.

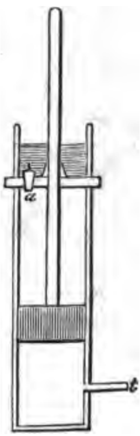
In practice it is very convenient to have two such barrels or cylinders arranged side by side, the piston-rods of which are formed into racks, having

Fig. 9.



a pinion, or small toothed wheel between them, moved by a winch. By this contrivance the operation of exhaustion is much facilitated and the labor lessened. The arrangement is shown in fig. 9.

Fig. 10.



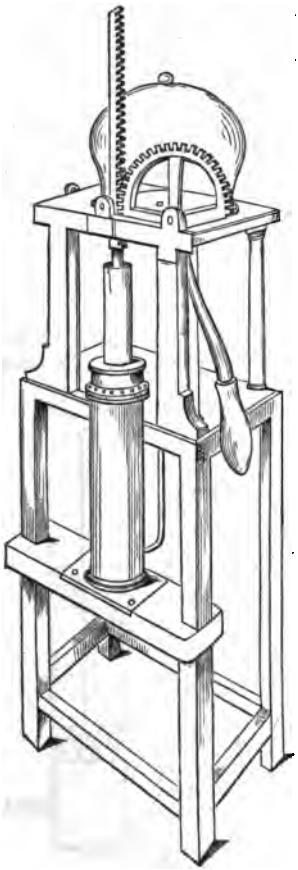
A simpler and far superior form of air-pump is thus constructed; the cylinder, which may be of large dimensions, is furnished with an accurately fitted solid piston, the rod of which moves, air tight, through a contrivance called a stuffing-box, at the top of the cylinder, where also the only valve *essential* to the apparatus is to be found; this latter is a solid conical plug of metal, shown at *a* in the figure, kept tight by the oil contained in the chamber into which it opens. The communication with the vessel to be exhausted is made by a tube which enters the cylinder a little above the bottom. The action is the following: let the piston be supposed in the act of rising from the bottom of the cylinder; as soon as it passes the mouth of the tube *t*, (fig. 10,) all communication is stopped between the air above the piston and the vessel to be exhausted; the enclosed air suffers compression, until it acquires sufficient elasticity to lift the metal valve and escape by bubbling through the oil. When the piston makes its descent, and this valve closes, a vacuum is left in the upper part of the cylinder, into which the air of the receiver rushes so soon as the piston has passed below the orifice of the connecting tube.

In the silk valved air-pump exhaustion ceases when the elasticity of the air in the receiver becomes too feeble to raise the valve; in that last described, the exhaustion may, on the contrary,

be carried to an indefinite extent, without, however, under the most favourable circumstances, becoming complete. The conical valve is made to project a little below the cover of the cylinder, so as to be forced up by the piston when the latter reaches the top of the cylinder; the oil then enters and displaces any air that may be lurking in the cavity.

It is a great improvement to the machine to supply the piston with a *relief-valve* opening upwards; this may also be of metal, and contained within the body of the piston. Its use is to avoid the momentary condensation of the air in the receiver when the piston descends. The pump is worked by a lever in the manner represented in the drawing below.

Fig. 11.



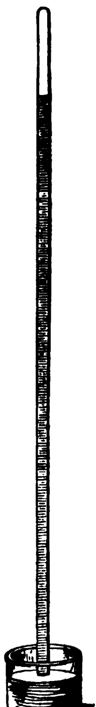
To return to the atmosphere. Air possesses weight: a light flask or globe of glass, furnished with a stop-cock and exhausted by the air-pump, weighs considerably less than when full of air. If the capacity of the vessel be equal to 100 cubic inches, this difference amounts to nearly 30 grains.

The mere fact of the pressure of the atmosphere may be demonstrated by securely tying a piece of bladder over the mouth of an open glass receiver, and then exhausting the air from beneath it; the bladder will become more and more concave, until it suddenly breaks. A thin square glass bottle, or a large air tight tin box may be crushed by withdrawing the support of the air in the inside. Steam-boilers have been often destroyed in this manner by collapse, in consequence of the accidental formation of a partial vacuum within.

After what has been said on the subject of fluid pressure, it will scarcely be necessary to observe that the law of equality of pressure in all directions also holds good in the case of the atmosphere. The perfect mobility of the particles of air permits the transmission of the force generated by their gravity. The sides and bottom of an exhausted vessel are pressed upon with as much force as the top.

If a glass tube of considerable length could be perfectly exhausted of air, and then held in an upright position, with one of its ends dipping into a vessel of liquid, the latter, on being allowed access to the tube, would rise in its interior until the weight of the column balanced the pressure of the air upon the surface of the liquid. Now if the density of this liquid were known, and the height and area of the column measured, means would be furnished for exactly estimating the amount of pressure exerted by the atmosphere.

Fig. 12.



Such an instrument is the barometer: a straight glass tube is taken, about 36 inches in length, and sealed by the blow-pipe flame at one extremity; it is then filled with clean, dry mercury, care being taken to displace all air-bubbles, the open end stopped with a finger, and the tube inverted in a basin of mercury. On removing the finger, the fluid sinks away from the top of the tube, until it stands at the height of about 30 inches above the level of that in the basin. Here it remains supported by, and balancing the atmospheric pressure, the space above the mercury in the tube being of necessity empty.

The pressure of the atmosphere is thus seen to be capable of sustaining a column of mercury thirty inches in height, or thereabouts; now such a column, having an area of one inch, weighs between 14 and 15 pounds, consequently such must be the amount of the pressure exerted upon every square inch of the surface of the earth, and of the objects situated thereon, at least near the level of the sea. This enormous force is borne without inconvenience by the animal frame, by reason of its perfect uniformity in every direction, and it may be doubled, or even tripled without injury.

A barometer may be constructed with other liquids besides mercury; but as the height of the column must always bear an inverse proportion to the density of the liquid, the length of tube required will be often considerable; in the case of water it will exceed 33 feet. It is seldom that any other liquid than mercury is employed in the construction of this instrument.

It will now be necessary to consider a most important law which connects the volume occupied by a gas with the pressure made upon it, and which is thus expressed:—

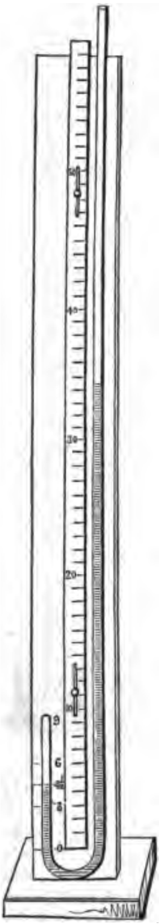
> The volume of a gas is *inversely* as the pressure: the density and elastic force are *directly* as the pressure, and *inversely* as the volume.

For instance, 100 cubic inches of gas under a pressure of 30 inches of mercury would expand to 200 cubic inches were the pressure reduced to one half, and shrink, on the contrary, to 50 cubic inches if the original were doubled. The increase of density must necessarily be in direct proportion to the pressure, and the elastic force follows the same rule.

This, which is usually called the law of Mariotte, is easily demonstrable by direct experiment. A glass tube, about 7 feet in length, is closed at one end, and bent into the form represented, (fig. 13,) the open limb of the siphon being the longest. It is next attached to a board furnished with a movable scale of inches, and enough mercury is introduced to fill the bend, the level being evenly adjusted, and marked upon the board. Mercury is now poured into the tube until it is found that the enclosed air has been reduced to one-half of its former volume; and on applying the scale, it will be found that the level of the mercury in the open part of the tube stands very nearly 30 inches above that in the closed portion. The pressure of an additional "atmosphere" has consequently reduced the bulk of the contained air to one half. If the experiment be still continued until the volume of air is reduced to a third, it will be found that the column measures 60 inches, and so in like proportion as far as the experiment is carried.

This instrument is better adapted for illustration of the principle than for furnishing rigorous proof of the law; this has, however, been done. MM. Arago and Dulong published, in the year 1830, an account of certain

Fig. 13.



experiments made by them in Paris, in which the law in question had been verified to the extent of 27 atmospheres.

All gases are alike subject to this law, and all vapors of volatile liquids, when remote from their points of condensation.* It is a matter of the greatest importance in practical chemistry, since it gives the means of making corrections for pressure, or determining by calculation the change of volume which a gas would suffer by any given change of external pressure.

Let it be required, for example, to solve the following problem: We have 100 cubic inches of gas in a graduated jar, the barometer standing at 29 inches; how many cubic inches will it occupy when the column rises to 30 inches? Now the volume must be inversely as the pressure; consequently a change of pressure in the proportion of 29 to 30 must be accompanied by a change of volume in the proportion of 30 to 29; 30 cubic inches of gas contracting to 29 cubic inches under the conditions imagined. Hence the answer:

$$30 : 29 :: 100 : 96{\cdot}67 \text{ cubic inches.}$$

The reverse of the operation will be obvious.

From what has been said respecting the easy compressibility of gases, it will be easily seen that the atmosphere cannot have the same density, and cannot exert equal pressures at different elevations above the sea-level, but that, on the contrary, these must diminish with the altitude, and very rapidly. The lower strata of air have to bear the weight of those above them; they become in consequence denser and more compressed than the upper portions. The following table, which is taken from Mr. Graham's work, shows in a very simple manner the rule followed in this respect.

Height above the sea in miles.	Volume of air.	Height of barometer in inches.
0	1	30
2·905	2	15
5·41	4	7·5
8·115	8	3·75
10·82	16	1·875
13·525	32	·9375
16·23	64	·46875

The numbers in the first column form an *arithmetical* series, by the constant addition of 2·705; those in the second column an increasing *geometrical* series, each being the double of its predecessor; and those in the third, a decreasing geometrical series, in which each number is the half of that standing above it.

* When near the condensing point the law no longer holds; the volume diminishes *more rapidly* than the theory indicates, a smaller amount of pressure being then sufficient.

In ascending into the air in a balloon these effects are well observed; the expansion of the gas within the machine, and the fall of the mercury in the barometer, soon indicate to the voyager the fact of his having left below him a considerable part of the whole atmosphere.

Fig. 14.

The invention of the barometer, which took place in the year 1643 by Torricelli, a pupil of the celebrated Galileo, speedily led to the observation that the atmospheric pressure at the same level is not constant, but possesses, on the contrary, a small range of variation, seldom exceeding in Europe, 2 or 2·5 inches, and within the tropics usually confined within much narrower limits. Two kinds of variations are distinguished; regular or horary, and irregular or accidental. It has been observed, that in Europe the height of the barometer is greatest at two periods in the twenty-four hours, depending upon the season. In winter the first maximum takes place about 9 A. M., the first minimum at 3 P. M., after which the mercury again rises and attains its greatest elevation at 9 in the evening; in summer these hours of the aerial tides are somewhat altered. The accidental variations are much greater in amount, and render it extremely difficult to trace the regular changes above-mentioned.

The barometer is applied with great advantage to the measurement of accessible heights, and it is also in daily use for foretelling the state of the weather; its indications are in this respect extremely deceptive, except in the case of sudden and violent storms, which are almost always preceded by a rapid fall in the mercurial column.

To the practical chemist, a moderately good barometer is an indispensable article, since in all experiments in which volumes of gases are to be estimated, an account must be taken of the state of the pressure of the atmosphere. The marginal drawing represents a very convenient and economical siphon-barometer for this purpose. A piece of new and stout tube, of about one-third of an inch in internal diameter, is procured at the glass-house, sealed at one extremity, and bent into the siphon form, as represented. Pure and warm mercury is next introduced by successive portions until the tube is completely filled, and the latter being held in an upright position, the level of the metal in the lower and open limb is conveniently adjusted by displacing a portion by a stick or glass rod. The barometer is, lastly, attached to a board, and furnished with a long scale, made to slide, which may be of box-wood, with a slip of ivory at each end. When an observation is to be taken, the lower extremity, or zero of the scale, is placed exactly even with the mercury in the short limb, and then the height of the column at once read off.

HEAT.

It will be convenient to consider the subject of Heat under several sections, and in the following order:

1. Expansion of bodies, or effects of variations of temperature in altering their dimensions.
2. Conduction, or transmission of heat.
3. Change of state.
4. Capacity of bodies for heat.

The phenomena of radiation must be deferred until a sketch has been given of the science of light.

EXPANSION.

If a bar of metal be taken, of such magnitude as to fit accurately to a gauge when cold, heated considerably, and again applied to the gauge, it will be found to have become enlarged in all its dimensions. When cold, it will once more enter the gauge.

Again, if a quantity of liquid contained in a glass bulb, furnished with a narrow neck, be plunged into hot water, or exposed to any other source of

Fig. 15.

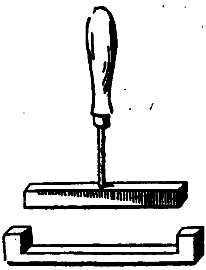
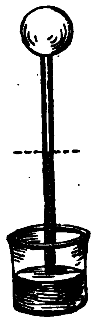


Fig. 16.

Fig. 17.



heat, the liquid will mount in the stem, showing that its volume has been increased.

Or, if a portion of air be confined in any vessel, the application of a slight degree of heat will suffice to make it occupy a space sensibly larger. This most general of all the effects of heat furnishes in the outset a principle, by the aid of which an instrument can be constructed capable of taking cognizance of changes of temperature in a manner equally accurate and convenient: such an instrument is the thermometer.

A capillary glass tube is chosen, of uniform diameter; one extremity is closed and expanded into a bulb, by the aid of the blow-pipe flame, and the other somewhat drawn out, and left open. The bulb is now cautiously heated by a spirit-lamp, and the open extremity plunged into a vessel of mercury, a

portion of which rises into the bulb when the latter cools, replacing the air which had been expanded and driven out by the heat. By again applying the flame, and causing this mercury to boil, the remainder of the air is easily expelled, and the whole space filled with mercurial vapor, on the condensation of which the metal is forced into the instrument by the pressure of the air until it becomes completely filled. The thermometer thus filled is now to be heated until so much mercury has been driven out by the expansion of the remainder, that its level in the tube shall stand at common temperatures at the point required. This being satisfactorily adjusted, the heat is once more applied, until the column rises quite to the top; and then the extremity of the tube is hermetically sealed by the blow-pipe. The retraction of the mercury on cooling now leaves an empty space in the upper part of the tube, which is essential to the perfection of the instrument.

The thermometer is yet to be graduated; and to make its indications comparable with those of other instruments, a scale, having certain fixed points, at the least two in number, must be adapted to it.

It has been observed, that the temperature of melting ice, that is to say, of a mixture of ice and water, is always constant; a thermometer, already graduated, plunged into such a mixture, always marks the same degree of temperature, and a simple tube filled in the manner described, and so treated, exhibits the same effect in the unchanged height of the little mercurial column, when tried from day to day. The freezing-point of water, or melting-point of ice, constitutes then one of the invariable temperatures demanded.

Another is to be found in the boiling-point of water, which is always the same under similar circumstances. A clean metallic vessel is taken, into which pure water is put and made to boil; a thermometer placed in the boiling liquid invariably marks the same degree of temperature so long as the height of the barometer remains unchanged.

The tube having been carefully marked with a file at these two points, it remains to divide the interval into degrees; this is entirely arbitrary. In France, and throughout the greater part of Germany, the scale called *centigrade* is employed; the space in question being divided into 100 parts, the zero being placed at the freezing-point of water. The scale is continued above and below these points, numbers below 0 being distinguished by the negative sign.

In England the very inconvenient division of Fahrenheit is everywhere in use; the above space is divided into 180 degrees, but the zero, instead of starting from the freezing-point of water, is placed 32 degrees below it, so that the temperature of ebullition is expressed by the number 212°.

The plan of Reaumur is nearly confined to the north of Germany and Russia; in this scale the freezing-point of water, is made 0°, and the boiling point 80°.

It is unfortunate that a uniform system has not been generally adopted in graduating thermometers; this would render unnecessary the labor which now so frequently has to be performed of translating the language of one scale into that of another. To effect this presents, however, no great difficulty. Let it be required, for example, to know the degree on Fahrenheit's scale, which corresponds to 60° centigrade.

$$100^\circ \text{ cent.} = 180^\circ \text{ Fahr. or } 5^\circ \text{ cent.} = 9^\circ \text{ Fahr.}$$

Consequently

$$5 : 9 :: 60 : 108$$

But then as Fahrenheit's scale commences with 32° instead of 0°, that number must be added to the result, making 60° cent. = 140° Fahrenheit.

The rule then will be the following: To convert centigrade degrees into

Fahrenheit degrees, multiply by 9, divide the product by 5, and add 32; to convert Fahrenheit degrees into centigrade degrees, subtract 32, multiply by 5, and divide by 9.

Mercury is usually chosen for making thermometers on account of its regularity of expansion within certain limits, and because it is easy to have the scale of great extent from the large interval between the freezing and boiling-points of the metal. Other substances are sometimes used; alcohol is employed for estimating very low temperatures.

Air-thermometers are also used for some few particular purposes; indeed the first thermometer ever made was of this kind. There are two modifications of this instrument; in the first, the liquid into which the tube dips is open to the air, and in the second, shown below, the atmosphere is completely excluded. The effects of expansion are in the one case complicated with those arising from changes of pressure, and in the other, cease to be visible at all when the whole instrument is subjected to alterations of temperature, because the air in the upper and lower reservoir being equally affected by

Fig. 18.

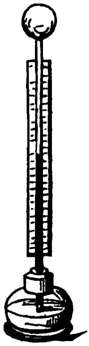
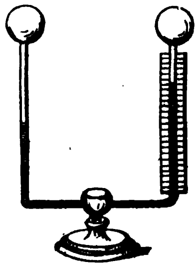


Fig. 19.



such changes, no alteration in the height of the fluid column can occur. Accordingly, such instruments are called *differential* thermometers, since they serve to measure differences of temperatures between the two portions of air, while changes affecting both alike are not indicated. Fig. 19 shows another form of the same instrument.

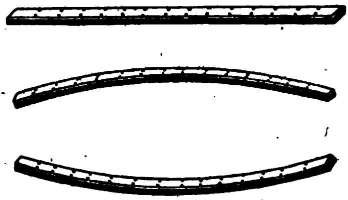
The air-thermometer may be employed for measuring all temperatures, from the lowest to the highest; M. Pouillet has described one by which the heat of an air-furnace could be measured. The reservoir of this instrument is of platinum, and it is connected with a piece of apparatus, by which the increase of volume experienced by the included air is determined.

All bodies are enlarged in their dimensions by the application of heat, and reduced by its abstraction, or, in other words, contract, on being artificially cooled; this effect takes place to a comparatively small extent with solids, to a larger amount in liquids, and most of all in the case of gases. This is the general rule; an exception is nevertheless to be found in certain curious liquids, which result from the condensation of gases, whose expansibility exceeds that of the gases themselves.

Each solid and liquid has a rate of expansion peculiar to itself; gases, on the contrary, all expand alike for the same increase of heat.

The difference of expansibility among solids is very easily illustrated by the following arrangement: A thin straight bar of iron is firmly fixed, by numerous rivets, to a similar bar of brass; so long as the temperature at which the two metals were united remains unchanged, the compound bar preserves its straight figure; but any alteration of temperature gives rise to a

Fig. 20.



corresponding curvature. Brass is more dilatable than iron; if the bar be heated, therefore, the former expands more than the latter, and forces the straight bar into a curve, whose convex side is the brass; if it be artificially cooled, the brass contracts more than the iron, and the reverse of this effect is produced.

This fact has received a most valuable application. It is not necessary to insist on the importance of possessing instruments for the accurate measurement of time; such are absolutely indispensable to the successful cultivation of astronomical science, and not less useful to the navigator from the assistance they give him in finding the longitude at sea. For a long time, notwithstanding the perfection of finish and adjustment bestowed upon clocks and watches, an apparently insurmountable obstacle presented itself to their uniform and regular movement; this obstacle was the change of dimensions, to which the regulating parts of the machine were subject by alterations of temperature. A clock may be defined as an instrument for registering the number of beats made by a pendulum; now the time of oscillation of a pendulum depends *principally* upon its length; any alteration in this condition will seriously affect the rate of the clock. The material of which the rod of the pendulum is composed is subject to expansion and contraction by changes of temperature; so that a pendulum adjusted to vibrate seconds at 60°, would go too slow when the temperature rose to 70°, from its elongation, and too fast when the temperature fell to 50° from the opposite cause

Fig. 21.

This great difficulty has been overcome; by making the rod of a number of bars of iron and brass, or iron and zinc, metals whose rates of expansion are different, and arranging these bars in such a manner that the expansion in one direction of the iron shall be exactly compensated by that in the opposite direction of the brass or zinc, it is possible to maintain under all circumstances of temperature an invariable distance between the points of suspension and of oscillation. This is often called the *gridiron pendulum;* the diagram in the margin will clearly illustrate its principle; the shaded bars are supposed to be iron and the others brass.

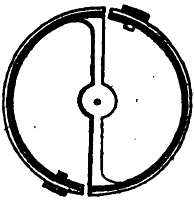
A still simpler compensation pendulum is thus constructed. The weight or bob, instead of being made of a disc of metal, consists of a cylin-

Fig. 22.

drical glass jar containing mercury, which is held by a stirrup at the extremity of the steel pendulum rod. The same increase of temperature which lengthens this rod, causes the volume of the mercury to enlarge, and its level to rise in the jar; the centre of gravity is thus elevated, and by properly adjusting the quantity of mercury in the glass, the virtual length of the pendulum may be made constant.

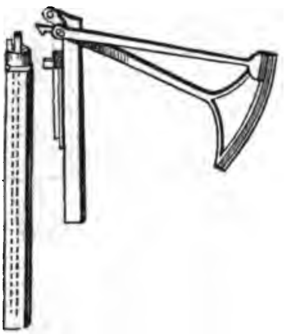
In watches the governing power is a horizontal weighted wheel, set in motion in one direction by the machine itself, and in the other by a fine spiral spring. The rate of going depends greatly on the diameter of this wheel, and the diameter is of necessity subject to variation by change of temperature. To remedy the evil thus involved, the circumference of the balance-wheel is made of two metals having different rates of expansion, fast soldered together, the most expansible being on the outside. The compound rim is also cut through in two or more places, as represented in the drawing. When the watch is exposed to a high temperature, and the diameter of the wheel becomes enlarged by expansion, each segment is made, by the same agency, to assume a sharper curve, whereby its centre of gravity is thrown inwards, and the expansive effect compensated. Many other beautiful applications of the same principle might be pointed out; the metallic thermometer of M. Breguet is one of these.

Fig. 23.



Mr. Daniell has very skilfully applied the expansion of a rod of metal to the measurement of temperatures above those capable of being taken by the thermometer. A rod of iron or platinum, about five inches long, is dropped into a tube of black-lead ware; a little cylinder of baked porcelain is put over it, and secured in its place by a platinum strap and a wedge of porcelain. When the whole is exposed to heat, the expansion of the bar drives forward the cylinder, which moves with a certain degree of friction, and shows, by the extent of its displacement, the lengthening which the bar had undergone. It remains, therefore, to measure the amount of this displacement, which must be very small, even when the heat had been exceedingly intense. This is effected by the contrivance shown in the drawing, in which the motion of the longer arm of the lever carrying the vernier of the scale is multiplied by ten, in consequence of its superior length. The scale itself is made comparable with that of the ordinary thermometer, by plunging the instrument into a bath of mercury near its point of congelation, and afterwards into another of the same metal in a boiling state, and marking off the interval. By this instrument the melting point of cast iron was fixed at 2786° Fahrenheit, and the greatest heat of a good wind-furnace at about 3300°.

Fig. 24.



The actual amount of expansion which different solids undergo by the same

increase of heat, has been carefully investigated. The following are some of the results obtained by MM. Lavoisier and Laplace. The fraction indicates the amount of expansion in length suffered by rods of the under mentioned bodies in passing from 32° to 212°.

English flint glass	$\frac{1}{1248}$	Soft iron	$\frac{1}{819}$
Common French glass	$\frac{1}{1147}$	Gold	$\frac{1}{682}$
Glass without lead	$\frac{1}{1142}$	Copper	$\frac{1}{581}$
Another specimen	$\frac{1}{1090}$	Brass	$\frac{1}{533}$
Steel untempered	$\frac{1}{927}$	Silver	$\frac{1}{524}$
Tempered steel	$\frac{1}{807}$	Lead	$\frac{1}{351}$

Metals appear to expand pretty uniformly for equal increments of heat within the limits stated, but above the boiling-point of water the rate of expansion becomes irregular and more rapid.

The force exerted in the act of expansion is very great; in laying down railways, building iron bridges, erecting long ranges of steam-pipes, and in executing all works of the kind in which metal is largely used, it is indispensable to make provision for these changes of dimensions.

A very useful little application of expansion by heat is that to the cutting of glass by a hot iron; this is constantly practised in the laboratory for a great variety of purposes. The glass to be cut is marked with ink in the wished-for direction, and then a crack commenced by any convenient method, at some distance from the desired line of fracture, may be led by the point of a heated iron rod along the latter with the greatest precision.

Expansion of fluids.—The dilatation of a fluid may be determined by filling with it a thermometer, in which the relation between the capacity of the ball and that of the stem is exactly known, and observing the height of the column at different temperatures. It is necessary in this experiment to take into account the effects of the expansion of the glass itself, the observed result being evidently the *difference* of the two.

Liquids vary exceedingly in this particular. The following table is taken from Péclet's *Elémens de Physique.*

Apparent dilatation in glass between 32° *and* 212°.

Water	$\frac{1}{22}$
Hydrochloric acid, sp. gr. 1·137	$\frac{1}{17}$
Nitric acid, sp. gr. 1·4	$\frac{1}{9}$
Sulphuric acid, sp. gr. 1·85	$\frac{1}{17}$
Ether	$\frac{1}{14}$
Olive oil	$\frac{1}{12}$
Alcohol	$\frac{1}{9}$
Mercury	$\frac{1}{64}$

The expansion is, for the most part, uniform between these temperatures; but beyond 212° it becomes irregular and increasing. This is well seen in the case of mercury.

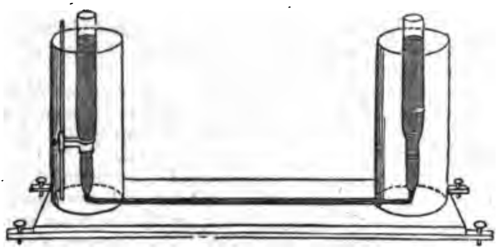
Absolute expansion of mercury for 180°

Between 32° and 212°	$\frac{1}{55\cdot5}$
Between 212° and 392°	$\frac{1}{54\cdot25}$
Between 392° and 572°	$\frac{1}{53}$

The absolute amount of expansion of mercury is, for many reasons, a point of great importance: it has been very carefully determined by a method independent of the expansion of the containing vessel. The apparatus employed

for this purpose by MM. Dulong and Petit is shown in fig. 25, divested, however, of many of its subordinate parts. It consists of two upright glass tubes, connected at their basis by a horizontal tube of much narrower dimensions. Since a free communication exists between the two tubes, mercury poured into the one will rise to the same level in the other, provided its temperature is the same in both tubes; when this is not the case, the hottest column will be the tallest, because the expansion of the metal diminishes its specific gravity, and the law of hydrostatic equilibrium requires that the heights of

Fig. 25.



such columns should be inversely as their densities. By the aid of the outer cylinders, one of the tubes is maintained constantly at 32°, while the other is raised, by means of heated water or oil, to any required temperature. The perpendicular heights of the columns may then be read off by a horizontal micrometer telescope, moving on a vertical divided scale.

These heights represent volumes of equal weight, because volumes of equal weight bear an inverse proportion to the densities of the liquids, so that the amount of expansion admits of being very easily calculated. Thus, let the column at 32° be 6 inches high, and that of 212° 6·108 inches, the increase in height, 108 on 6000, or $\frac{1}{55.5}$ part of the whole must represent the absolute cubical expansion.

The indications of the mercurial thermometer are inaccurate when high ranges of temperature are concerned, from the increased expansibility of the metal; on this account a certain correction is necessary in many experiments, and tables for this purpose have been drawn up.

An exception to the regularity of expansion in fluids exists in the case of water; it is so remarkable, and its consequences so important, that it is necessary to advert to it particularly.

Let a large thermometer-tube be filled with water at the common temperature of the air, and then artificially cooled. The liquid will then be observed to contract regularly, until the temperature falls to about 40°, or 8° above the freezing point. After this, a farther reduction of temperature causes expansion instead of contraction in the volume of the water, and this expansion continues until the liquid arrives at its point of congelation, when so sudden and violent an enlargement takes place, that the vessel is almost invariably broken. At the temperature of 40°, or more correctly, perhaps, 39° 5, water is at its maximum density; increase or diminution of heat produces upon it, for a short time, the same effect.

A beautiful experiment by Dr. Hope illustrates the same fact. If a tall jar filled with water at 50° or 60°, and having in it two small thermometers, one at the bottom and the other near the surface, be placed at rest in a very cold room, the following changes will be observed. The thermometer at the bot-

tom will fall more rapidly than that at the top, until it has attained the temperature of 40°, after which it will remain stationary. At length the upper thermometer will also mark 40°, but still continue to sink as rapidly as before, while that at the bottom remains stationary. It is easy to explain these effects: the water in the upper part of the jar is rapidly cooled by contact with the air; it becomes denser in consequence, and falls to the bottom, its place being supplied by the lighter and warmer liquid, which in its turn suffers the same change; and this circulation goes on until the whole mass of water has acquired its condition of maximum-density; that is, until the temperature has fallen to 40°. Beyond this, loss of heat occasions expansion instead of contraction, so that the very cold water on the surface has no tendency to sink, but rather the reverse.

This singular anamoly in the behavior of water is attended by the most beneficial consequences, in shielding the inhabitants of the waters from excessive cold.

Expansion of gases.—This is a point of great practical importance to the chemist, and, happily, we have very excellent evidence upon the subject. The following four propositions exhibit, at a single view, the principal facts of the case.

1. All gases expand alike for equal increments of heat; and all vapours, when remote from their condensing-points, follow the same law.
2. The rate of expansion is not altered by a change in the state of compression, or elastic force of the gas itself.
3. The rate of expansion is uniform for all degrees of heat.
4. The actual amount of expansion is equal to $\frac{1}{460}$th part of the volume of the gas at 0° Fahrenheit, for each degree of the same scale.*

It will be unnecessary to enter into any description of the methods of investigation by which these results have been obtained; the advanced student will find in Pouillet's *Elémens de Physique*, and in the papers of MM. Magnus† and Regnault‡ all the information he may require.

In the practical manipulation of gases, it very often becomes necessary to make a correction for temperature, or to discover how much the volume of a gas would be increased or diminished by a particular change of temperature; this can be effected with great facility. Let it be required, for example, to find the volume, which 100 cubic inches of any gas at 50° would become on the temperature rising to 60°.

The rate of expansion is $\frac{1}{460}$th of the volume at 0° for each degree; or 460 measures at 0° become 461 at 1°, 462 at 2°, $460+50=510$ at 50°, and $460+60=520$ at 60°. Hence

Meas. at 50°.		Meas. at 60°.		Meas. at 50°.		Meas. at 60°.
510	:	520	: :	100	:	101·96

This, and the correction for pressure, are operations of very frequent occurrence in chemical investigations, and the student will do well to become familiar with them.

Note.—Of the four propositions stated in the text, the first and second have quite recently been shown to be true within certain limits only; and the third, although in the highest degree probable, would be very difficult to demonstrate rigidly; in fact, the equal rate of expansion of air is assumed in all experi-

* Or, the amount of expansion is equal to $\frac{1}{493}$d part of the volume which the gas occupies at 32° F., for each degree of Fahrenheit's scale.—R. B.

† Poggendorf's Annalen, lv., p. 1.

‡ Ann. Chim. et Phys., 3d Series, iv. p. 5, and v. p. 52.

ments on other substances, and becomes the standard by which the results are measured.

The rate of expansion for the different gases is *not* absolutely the same, but the difference is so small that for most purposes it may with perfect safety be neglected. Neither is the state of elasticity altogether indifferent, the expansion being sensibly *greater* for an equal rise of temperature when the gas is in a compressed state.

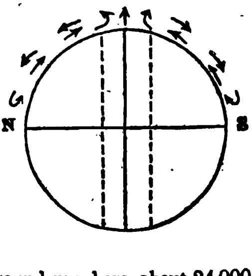
It is important to notice, that the greatest deviations from the rule are exhibited by those gases, which, as will hereafter be seen, are most easily liquefied, such as carbonic acid, cyanogen, and sulphurous acid, and that the discrepancies become smaller and smaller as the elastic force is lessened; so that if means existed for comparing the different gases in states *equally distant* from their points of condensation, there is reason to believe that the law would be strictly fulfilled.

The experiments of MM. Dulong and Petit give for the rate of expansion $\frac{1}{448}$th of the volume at 0°; this is no doubt too high. Those of Rudberg give $\frac{1}{461}$st part; of Magnus $\frac{1}{459}$th; and of Regnault $\frac{1}{458}$th; the fraction $\frac{1}{460}$th is adopted in the text as a convenient number, sufficiently near the mean of the three preceding, to answer all purposes.

The ready expansibility of air by heat gives rise to the phenomena of winds; in the temperate regions of the earth these are very variable and uncertain, but within and near the tropics a much greater regularity prevails;—of this the *trade-winds* furnish a beautiful example.

The smaller degree of obliquity with which the sun's rays fall in the localities mentioned, occasions the broad belt thus stretching round the earth to become more heated than any other part of the surface. The heat thus acquired by absorption is imparted to the lowest stratum of air, which, becoming expanded, rises, and gives place to another, and in this manner an ascending current is established,—the colder and heavier air streaming in laterally from the more temperate regions, north and south, to supply the partial vacuum thus occasioned. A circulation so commenced will be completed in obedience to the laws of hydrostatics, by the establishment of counter-currents in the higher parts of the atmosphere, having directions the reverse of those on the surface.

Fig. 26.



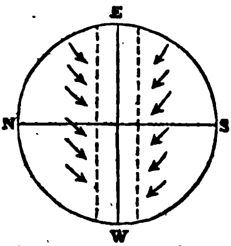
Such is the effect produced by the unequal heating of the equatorial parts, or, more correctly, such would be the effect were it not greatly modified by the earth's movement of rotation.

As the circumference of the earth is, in round numbers, about 24,000 miles, and since it rotates on its axis, from west to east, once in 24 hours, the equatorial parts must have a motion of 1000 miles per hour; this velocity diminishes rapidly towards each pole, where it is reduced to nothing.

The earth in its rotation carries with it the atmosphere, whose velocity of movement corresponds, in the absence of disturbing causes, with that part of the surface immediately below it. The air which rushes towards the equator, to supply the place of that raised aloft by its diminished density, brings with

it the degree of momentum belonging to that portion of the earth's surface from which it set out, and as this momentum is less than that of the earth, under its new position, the earth itself travels faster than the air immediately over it, thus producing the effect of a wind blowing in a contrary direction to that of its own motion. The original north and south winds are thus deviated from their primitive directions, and made to blow more or less from the eastward, so that the combined effects of the unequal heating and of the movement of rotation is to generate in the northern hemisphere a constant north-east wind, and in the southern hemisphere an equally constant south-east wind.

Fig. 27.



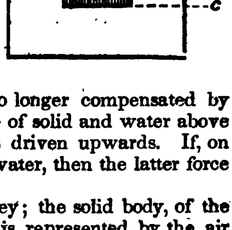
In the same manner the upper or return-current is subject to a change of direction in the reverse order; the rapidly moving wind of the tropics, transferred laterally towards the poles, is soon found to travel faster than the earth beneath it, producing the effect of a westerly wind, which modifies the primary current.

The trade-winds, it may be remarked, furnish an admirable physical proof of the reality of the earth's movement of rotation.

The theory of the action of chimneys, and of natural and artificial ventilation, belongs to the same subject.

Let the reader turn to the demonstration given of the Archimedean hydrostatic theorem: let him once more imagine a body immersed in water, and having a density equal to that of the water; it will remain in equilibrium in any part beneath the surface, and for these reasons:—The force which presses it downwards is the weight of the body added to the weight of the column of water above it; the force which presses it upwards is the weight of a column of water equal to the height of both conjoined;—the density of the body is that of water, that is, it weighs as much as an equal bulk of that liquid; consequently, the downward and upward forces are equally balanced, and the body remains at rest.

Fig. 28.



Next, let the circumstances be altered; let the body be lighter than an equal bulk of water; the pressure upwards of the column of water, *a c* is no longer compensated by the downward pressure of the corresponding column of solid and water above it; the former force preponderates, and the body is driven upwards. If, on the contrary, the body be specifically heavier than water, then the latter force has the ascendency, and the body sinks.

All things so described exist in a common chimney; the solid body, of the same density as that of the fluid in which it floats, is represented by the air in the chimney-funnel; the space *a b* represents the whole atmosphere above it. When the air inside and outside the chimney is at the same temperature, equilibrium takes place, because the downward tendency of the air within is counteracted by the upward pressure of that without.

Now, let the chimney be heated; the air suffers expansion, and a portion is expelled: the chimney therefore contains a smaller weight of air than it did before; the external and internal columns no longer balance each other, and the warmer and lighter air is forced upwards from below, and its place sup-

plied by cold air. If the brickwork, or other material of which the chimney is constructed, retain its temperature, this second portion of air is disposed of like the first, and the ascending current continues, so long as the sides of the chimney are hotter than the surrounding air.

Sometimes, owing to sudden changes of temperature in the atmosphere, the chimney may happen to be colder than the air about it. The column within forthwith suffers contraction of volume; the deficiency is filled up from without, and the column becomes heavier than one of similar height on the outside; the result is, that it falls out of the chimney, just as the heavy body sinks in the water, and has its place occupied by air from above. A descending current is thus produced which may be often noticed in the summer time by the smoke from neighboring chimneys finding its way into rooms, which have been for a considerable period without fire.

The ventilation of mines has long been conducted upon the same principle, and more recently it has been applied to dwelling-houses and assembly-rooms. The mine is furnished with two shafts, or with one shaft, divided throughout by a diaphragm of boards; and these are so arranged, that air forced down the one shall traverse the whole extent of the workings before it escapes by the other. A fire kept in one of these shafts, by rarefying the air within and causing an ascending current, occasions fresh air to traverse every part of the mine, and sweep before it the noxious gases, but too frequently present.

CONDUCTION OF HEAT.

Different bodies possess very different conducting powers with respect to heat: if two similar rods, the one of iron and the other of glass, be held in the flame of a spirit lamp, the iron will soon become too hot to be touched, while the glass may be grasped with impunity, within an inch of the red-hot portion.

Experiments made by analogous, but more accurate methods, have established a numerical comparison of the conducting powers of many bodies; the following may be taken as a specimen:

Gold	1000	Tin	304
Silver	973	Lead	179
Copper	898	Marble	23·6
Iron	374	Porcelain	12·2
Zinc	363	Fire-clay	11·4

As a class, the metals are by very far the best conductors, although much difference exists between them; stones, dense woods, and charcoal, follow next in order; then liquids in general, and gases, whose conducting power is almost inappreciable.

Under favorable circumstances, nevertheless, both liquids and gases may become rapidly heated; heat applied to the bottom of the containing vessel is very speedily communicated to its contents; this, however, is not so much by conduction, as by convection, or carrying. A complete circulation is set up; the portions in contact with the bottom of the vessel get heated, become lighter, and rise to the surface, and in this way the heat becomes communicated to the whole. If these movements be prevented by dividing the vessel into a great number of compartments, the really low conducting power of the substance is made evident, and this is the reason why certain organic fabrics, as wool, silk, feathers, and porous bodies in general, the cavities of which are full of air, exhibit such feeble powers of conduction.

The circulation of heated water through pipes is now extensively applied to the warming of buildings and conservatories, and in chemical works a

serpentine metal tube containing hot oil is often used for heating stills and evaporating pans; the two extremities of the tube are connected with the ends of another spiral built into a small furnace at a lower level, and an unintermitting circulation of the liquid takes place as long as heat is applied.

CHANGE OF STATE.

If equal weights of water at 32° and water at 174° be mixed, the temperature of the mixture will be the mean of the two temperatures, or 103. If the same experiment be repeated with snow, or finely powdered ice, at 32°, and water at 174°, the temperature of the whole will be still only 32°, *but the ice will have been melted.*

$$\left.\begin{array}{l}\text{1 lb. of water at } 32^\circ \\ \text{1 lb. of water at } 174^\circ\end{array}\right\} = \text{2 lbs. water at } 103^\circ.$$

$$\left.\begin{array}{l}\text{1 lb. of ice at } 32^\circ \\ \text{1 lb. of water at } 174^\circ\end{array}\right\} = \text{2 lbs. water at } 32^\circ.$$

In the last experiment, therefore, as much heat has been apparently lost as would have raised a quantity of water equal to that of the ice through a range of 142°.

The heat, thus become insensible to the thermometer in effecting the liquefaction of the ice, is called latent heat, or, better, heat of fluidity.

Again, let a perfectly uniform source of heat be imagined, of such intensity that a pound of water placed over it would have its temperature raised 10° per minute. Starting with water at 32°, in rather more than 14 minutes its temperature would have risen to 174°; but the same quantity of ice at 32°, exposed for the same interval of time, would not have its temperature raised a single degree. But then it would have become water; the heat received would have been exclusively employed in effecting the change of state.

This heat is not lost, for when the water freezes it is again evolved. If a tall jar of water, covered to exclude dust, be placed in a situation where it shall be quite undisturbed, and at the same time exposed to great cold, the temperature of the water may be reduced 10° or more below its freezing-point without the formation of ice; but then, if a little agitation be communicated to the jar, or a grain of sand dropped into the water, a portion instantly solidifies, and the temperature of the whole rises to 32°; the heat disengaged by the freezing of a small portion of the water will have been sufficient to raise the whole contents of the jar 10°.

The law thus illustrated in the case of water, is perfectly general. Whenever a solid becomes a liquid, a certain fixed and definite amount of heat disappears, or becomes latent; and conversely, whenever a liquid becomes a solid, heat to a corresponding extent is given out. The amount of latent heat varies much with different substances, as will be seen by the table:

Water* . . .	142°	Zinc . . .	493°
Sulphur . . .	145	Tin . . .	500
Lead . . .	162	Bismuth . . .	550

When a solid substance can be made to liquefy by a weak chemical attraction, cold results, from sensible heat becoming latent. This is the principle of the many frigorific mixtures to be found described in some of the older chemical treatises. When snow or powdered ice is mixed with common salt, and a thermometer plunged into the mass, the mercury sinks to 0°, while

* MM. De la Provostaye and Regnault, Ann. Chim. et Phys., 3d Series, viii. p. 1

the whole, after a short period, becomes fluid by the attraction between the water and the salt; such a mixture is very often used in chemical experiments to cool receivers and condense the vapours of volatile liquids. Powdered crystallized chloride of calcium and snow produce cold enough to freeze mercury. Even powdered nitrate of potash, or sal-ammoniac, dissolved in water, occasions a very notable depression of temperature; in every case, in short, in which solution is unaccompanied by energetic chemical action, cold is produced.

No relation is to be traced between the actual melting-point of a substance, and its latent heat when in a fused state.

A law of exactly the same kind as that described effects universally the gaseous condition; change of state from solid or liquid to gas, is accompanied by absorption of sensible heat, and the reverse, by its disengagement. The latent heat of steam and other vapors may be ascertained by a similar mode of investigation to that employed in the case of water.

When water at 32° is mixed with an equal weight of water at 212°, the whole is found to possess the mean of the two temperatures, or 122°; on the other hand, 1 part by weight of *steam* at 212° when condensed into cold water, is found to be capable of raising 5·6 parts of the latter from the freezing to the boiling-point, or through a range of 180°. Now $180 \times 5{\cdot}6 = 1008$; that is to say, steam at 212° in becoming water at 212° parts with enough heat to raise a weight of water equal to its own (if it were possible) 1008° of the thermometer. When water passes into steam, the same quantity of sensible heat becomes latent.

The vapors of other liquids seem to have less latent heat than that of water; the following table is by Dr. Ure, and serves well to illustrate this point.

Vapor of	water	967°
"	alcohol	442
"	ether	302
"	petroleum	178
"	oil of turpentine	178
"	nitric acid	532
"	liquor ammoniæ	837
"	vinegar	875

Ebullition is occasioned by the formation of bubbles of vapor within the body of the evaporating liquid, which rise to the surface and there break like bubbles of permanent gas. This occurs in different liquids at very different temperatures; under the same circumstances, the boiling-point is quite constant, and often becomes a physical character of great importance in distinguishing liquids which much resemble each other. A few cases may be cited in illustration:

Substance.	Boiling-point.
Ether	96°
Sulphuret of carbon	116
Alcohol	172
Water	212
Nitric acid, strong	248
Oil of turpentine	314
Sulphuric acid	620
Whale oil	630
Mercury	662

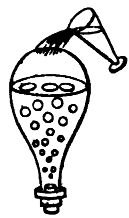
For ebullition to take place it is necessary that the elasticity of the vapor should be able to overcome the cohesion of the liquid and the pressure upon its surface; hence the extent to which the boiling-point may be modified.

Water, under the usual pressure of the atmosphere, boils at 212°; in a partially exhausted receiver, or on a mountain-top it boils at a much lower temperature, and in the best vacuum of an excellent air-pump, over oil of vitriol, which absorbs the vapor, it will often enter into violent ebullition while ice is in the act of forming upon the surface.

On the other hand, water confined in a very strong metallic vessel may be restrained from boiling by the pressure of its own vapor to an almost unlimited extent; a temperature of 350° or 400° is very easily obtained, and, in fact, it is said that it may be made red-hot, and yet retain its fluidity.

There is a very simple and beautiful experiment illustrative of the effect of diminished pressure in depressing the boiling-point of a liquid. A little water is made to boil for a few minutes in a flask or retort placed over a lamp, until the air has been chased out, and the steam issues freely from the neck. A tightly-fitting cork is then inserted, and the lamp at the same moment withdrawn. When the ebullition ceases it may be renewed at pleasure for a considerable time by the affusion of cold water, which, by condensing the vapor within, occasions a partial vacuum.

Fig. 29.



The nature of the vessel, or rather, the state of its surface, exercises an influence upon the boiling-point, and this to a much greater extent than was formerly supposed It has long been noticed that in a metallic vessel water boils, under the same circumstances of pressure, at a temperature one or two degrees below that at which ebullition takes place in glass; but it has lately been shown* that by particular management a much greater difference can be observed. If two similar glass flasks be taken, the one coated in the inside with a film of shellac, and the other completely cleansed by hot sulphuric acid, water heated over a lamp in the first, will boil at 211°, while in the second it will often rise to 221°, or even higher; a momentary burst of vapor then ensues, and the thermometer sinks a few degrees, after which it rises again. In this state, the introduction of a few metallic filings, or angular fragments of any kind, occasions a lively disengagement of vapor, while the temperature sinks to 212°, and there remains stationary. These remarkable effects must be attributed to an attraction between the surface of the vessel and the liquid.

A cubic inch of water in becoming steam under the ordinary pressure of the atmosphere expands into 1696 cubic inches, or nearly a cubic foot.

Steam, *not in contact with water*, is affected by heat in precisely the same manner as the permanent gases; its rate of expansion and increase of elastic force are the same. When water is present, however, this is no longer the case, but, on the contrary, the elastic force increases in a far more rapid proportion.

This elastic force of steam in contact with water, at different temperatures, has been very carefully determined by MM. Arago and Dulong. The force is expressed in atmospheres; the absolute pressure upon any given surface can be easily calculated, allowing 14·6 lbs. to each atmosphere. The experiments were carried to 25 atmospheres, at which point the difficulties and danger become so great as to put a stop to the inquiry; the rest of the table is the result of calculations founded on the data so obtained.

* Marcet, Ann. Chim. et Phys., 3d Series, v. p. 449.

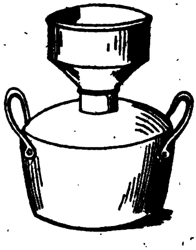
Pressure of steam in atmospheres.	Corresponding temp. Fahr.	Pressure of steam in atmospheres.	Corresponding temp. Fahr.
1	212°	13	381°
1·5	234	14	387
2	251	15	393
2·5	264	16	398
3	275	17	404
3·5	285	18	409
4	294	19	414
4·5	300	20	418
5	308	21	423
5·5	314	22	427
6	320	23	431
6·5	326	24	436
7	332	25	439
7·5	337	30	457
8	342	35	473
9	351	40	487
10	359	45	491
11	367	50	511
12	374		

It is a very remarkable fact, that the latent heat of steam diminishes as the temperature of the steam rises, so that equal weights of steam thrown into cold water exhibit the same heating power, although the actual temperature of the one portion may be 212° and that of the other 350° or 400°. This has also been found to be true at temperatures below the boiling-point; so that, it seems, to evaporate a given quantity of water the same *absolute* amount of heat is required whether it be performed slowly at the temperature of the air in a manner presently to be noticed, or whether it be boiled off under a pressure of 20 atmospheres. It is for this reason that the process of distillation in vacuo at a temperature which the hand can bear, so advantageous in other respects, can effect no *direct* saving of fuel.

The economical applications of steam are numerous and extremely valuable; they may be divided into two classes; those in which the heating power is employed, and those in which its elastic force is brought into use.

The value of steam as a source of heat depends upon the facility with which it may be conveyed to distant points, and upon the large amount of latent heat it contains, which is disengaged in the act of condensation. An invariable temperature of 212°, or higher, may be kept up in the pipes or other vessels in which the steam is contained by the expenditure of a very small quantity of the latter. Steam baths of various forms are used in the arts with great convenience, and also by the scientific chemist for drying filters and other objects where excessive heat would be hurtful; a very good instrument of the kind was contrived by Mr. Everitt. It is merely a small kettle, surmounted by a double box or jacket, into which the substance to be dried is put, and loosely covered by a card. The apparatus is placed over a lamp, and may be left without attention for many hours. A little hole in the side of the jacket gives vent to the excess of steam.

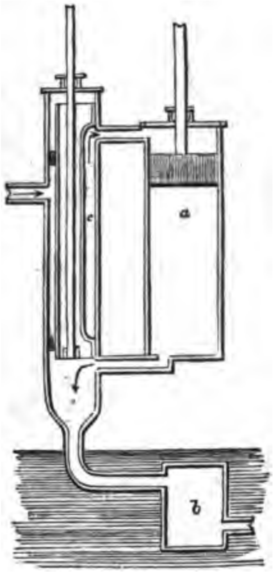
Fig. 30.



The principle of the steam-engine may be described in a few words; its

mechanical details do not belong to the design of the present volume. The machine consists essentially of a cylinder of metal, *a*, in which works a closely-fitting, solid piston, the rod of which passes, air-tight, through a stuffing-box at the top of the cylinder, and is connected with the machinery to be put in motion, directly, or by the intervention of an oscillating beam. A pipe communicates with the interior of the cylinder, and also with a vessel surrounded with cold water, called the condenser, marked *b* in the sketch, and into which a jet of cold water can at pleasure be introduced. A sliding-valve arrangement, shown at *c*, serves to open a communication between the boiler and the cylinder, and the cylinder and the condenser, in such a manner that while the steam is allowed to press with all its force upon one side of the piston, the other, open to the condenser, is necessarily vacuous. The valve is shifted by the engine itself at the proper moment, so that the piston is alternately driven by the steam up and down against a vacuum. A large air-pump, not shown in the engraving, is connected with the condenser, and serves to remove any air that may enter the cylinder, and also the water produced by condensation, together with that which may have been injected.

Fig. 31



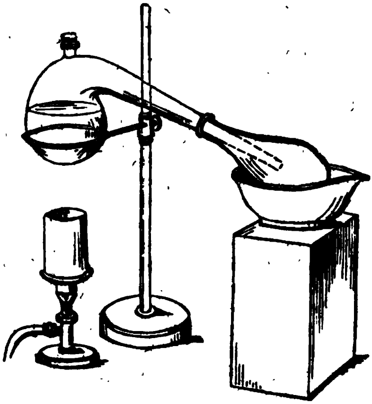
Such is the vacuum or condensing steam-engine. In what is called the high-pressure engine, the condenser and air-pump are suppressed, and the steam is allowed to escape at once from the cylinder into the atmosphere. It is obvious that in this arrangement the steam has to overcome the whole pressure of the air, and a much greater elastic force is required to produce the same effect; but this is to a very great extent compensated by the absence of the air-pump and the increased simplicity of the whole machine. Large engines, both on shore and in steam-ships, are usually constructed on the condensing principle, the pressure seldom exceeding six or seven pounds per square inch above that of the atmosphere; for small engines the high-pressure plan is, perhaps, preferable. Locomotive engines are of this kind.

There is a method of employing high-pressure steam with the common condensing engine, which has been long adopted in Cornwall, and is now getting into frequent use. The steam is cut off from the cylinder at one-third or less of the stroke, the movement of the piston being completed by the elasticity of that already admitted. The use of steam *expansively* in this way is said to effect great saving of fuel, which is still further economized by a peculiarity in the construction of the boilers of these engines. The constant objection to high pressure engines, the danger of explosion, will, perhaps, tend to prevent the general introduction of this improvement.

The process of distillation is very simple; its object is either to separate substances which rise in vapor at different temperatures, or to part a volatile liquid from a substance incapable of volatilization. The same process applied to bodies which pass directly from the solid to the gaseous condition, and the

reverse, is called *sublimation*. Every distillatory apparatus consists essentially of a boiler, in which the vapor is raised, and of a condenser, in which it returns to the liquid or solid condition. In the still employed for manufacturing purposes, the latter is usually a spiral metal tube immersed in a tub of water. The common retort and receiver constitute the simplest and most

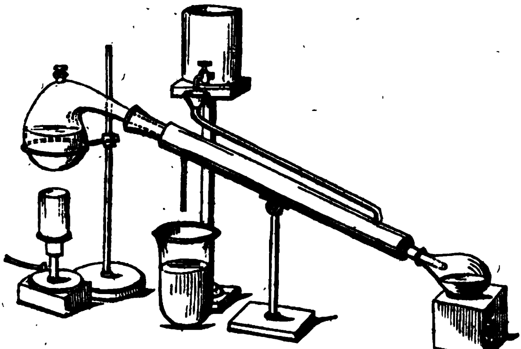
Fig. 32.



generally useful arrangement for distillation on the small scale; the retort is heated by a lamp or a charcoal fire, and the receiver is kept cool, if necessary, by a wet cloth, or it may be surrounded with ice.

The condenser of Professor Liebig is a very valuable instrument in the laboratory;—it consists of a glass tube tapering from end to end, fixed by perforated corks in the centre of a metal pipe, provided with tubes so arranged that a current of cold water may circulate through the apparatus. By putting a few pieces of ice into the little cistern, the temperature of this water may be kept at 32°, and extremely volatile liquids condensed.

Fig. 33.



Liquids evaporate at temperatures below their boiling-points; in this case the evaporation takes place solely from the surface. Water, or alcohol, exposed in an open vessel at the temperature of the air, gradually dries up and disappears; the more rapidly, the warmer and drier the air above it.

This fact was formerly explained by supposing that air and gases in general had the power of dissolving and holding in solution certain quantities of liquids, and that this power increased with the temperature; such an idea is incorrect.

Fig. 34.

If a barometer-tube be carefully filled with mercury and inverted in the usual manner, and then a few drops of water passed up the tube into the vacuum above, a very remarkable effect will be observed;—the mercury will be depressed to a small extent, and this depression will increase with increase of temperature. Now, as the space above the mercury is void of air, and the weight of the few drops of water quite inadequate to account for this depression, it must of necessity be imputed to the vapor which instantaneously rises from the water into the vacuum; and that this effect is really due to the elasticity or tension of the aqueous vapor, is easily proved by exposing the barometer to a heat of 212°, when the depression of the mercury will be complete, and it will stand at the same level within and without the tube, indicating that at that temperature the elasticity of the vapor is equal to that of the atmosphere;—a fact which the phenomenon of ebullition has already shown.

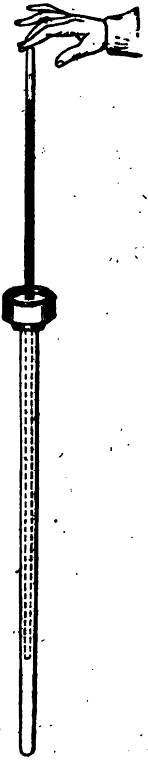
By placing over the barometer a wide open tube dipping into the mercury below, and then filling this tube with water at different temperatures, the tension of the aqueous vapor for each degree of the thermometer may be accurately determined by its depressing effect upon the mercurial column; the same power which forces the latter *down* one inch against the pressure of the atmosphere, would of course *elevate* a column of mercury to the same height against a vacuum, and in this way the tension may be very conveniently expressed. The following table was drawn up by Dr. Dalton, to whom we owe the method of investigation.

Temp.	Tension in inches of Mercury.	Temp.	Tension in inches of Mercury.
32°	·200	130°	4·34
40	·263	140	5·74
50	·375	150	7·42
60	·524	160	9·46
70	·721	170	12·13
80	1·000	180	15·15
90	1·360	190	19·00
100	1·860	200	23·64
110	2.530	212	30·00
120	3·330		

Other liquids tried in this manner are found to emit vapors of greater or less tension, for the same temperature according to their different degrees of volatility; thus a little ether introduced into the tube depresses the mercury 10 inches or more at the ordinary temperature of the air; oil of vitriol, on the other hand, does not emit any sensible quantity of vapor until a much greater heat is applied; and that given off by mercury itself in warm summer weather, although it may by very delicate means be detected, is far too little

to exercise any effect upon the barometer. In the case of water the evaporation is quite distinct and perceptible at the lowest temperatures, when frozen to solid ice in the barometer-tube; snow on the ground, or on a house-top, may often be noticed to vanish from the same cause day by day in the depth of winter, when melting is impossible.

Fig. 35.



There exists for each vapor a state of density which it cannot pass without losing its gaseous condition and becoming liquid; this point is called the condition of maximum density. When a volatile liquid is introduced in sufficient quantity into a vacuum, this condition is always reached, and then evaporation ceases. Any attempt to increase the specific gravity of this vapor by compressing it into a smaller space will be attended by the liquefaction of a portion, the density of the remainder being unchanged. If a little ether be introduced into a barometer, and the latter slowly sunk into a very deep cistern of mercury, it will be found that the height of the column in the tube above that in the cistern remains unaltered until the upper extremity of the barometer approaches the surface of the metal in the reservoir. It will be observed also, that as the tube sinks the little stratum of liquid ether increases in thickness, but no increase of elastic force occurs in the vapor above it, and, consequently, no increase of density, for tension and density are always directly proportionate to each other in the same vapor.

The point of maximum density of a vapor is dependent upon the temperature; it increases rapidly as the temperature rises. Thus, taking the specific gravity of atmospheric air at 212°=1000, that of aqueous vapor in its greatest possible state of compression for the temperature will be as follows:—

Temp.	Specific gravity.	Weight of 100 cubic inches.
32°	5·690	·136 grains
50	10·293	·247
60	14·108	·338
100	46·500	1·113
150	170·293	4.076
212	625·000	14·962

The last number was experimentally found by M. Gay-Lussac; the others are calculated upon that by the aid of Dr. Dalton's table of tensions.

Thus pressure, by causing an increase of density, may cause a vapor to assume a liquid form, the same effect is produced by cold, inasmuch as the latter depresses the point of maximum density.

For example, if 100 cubic inches of perfectly transparent and gaseous vapor of water at 100°, in the state above described, had its temperature reduced to 50°, not less than ·89* grain of fluid water would necessarily separate, or very nearly eight-tenths of the whole.

Evaporation into a space filled with air or gas follows the same law as evaporation into a vacuum: as much vapor rises, and the condition of maxi-

* 100 cubic inches aqueous vapors at 100° weighing 1·113 grains, would at 50° become educed to 90·1 cubic inches, weighing ·233 grains.

mum density is assumed in the same manner as if the space were perfectly empty; the sole difference lies in the length of time required. When a liquid evaporates into a vacuum the point of greatest density is attained at once, while in the other case some time elapses before this happens; the particles of air appear to oppose a sort of mechanical resistance to the rise of the vapor. The ultimate effect is, however, precisely the same.

When to a quantity of perfectly dry gas confined in a vessel closed by mercury, a little water is added, the latter immediately begins to evaporate, and after some time as much vapor will be found to have risen from it as if no gas had been present, the quantity depending entirely on the temperature to which the whole is subjected. The tension of this vapor will add itself to that of the gas and produce an expansion of volume, which will be indicated by an alteration of level in the mercury.

Vapor of water exists in the atmosphere at all times, and in all situations, and there plays a most important part in the economy of nature. The proportion of aqueous vapor present in the air is subject to great variation, and it often becomes exceedingly important to determine its quantity. This is easily done by the aid of the foregoing principles.

If the aqueous vapor be in its condition of greatest possible density for the temperature, or, as it is frequently but most incorrectly expressed, the air be saturated with vapor of water, the slightest reduction of temperature will cause the deposition of a portion in the liquid form. If, on the contrary, as is almost always in reality the case, the vapor of water be *below* its state of maximum density, that is, in an expanded condition, it is clear that a considerable fall of temperature may occur before liquefaction commences. The degree at which this takes place is called the dew-point, and it is determined with great facility by a very simple method. A little cup of thin tin-plate or silver, well polished, is filled with water at the temperature of the air, and a delicate thermometer inserted. The water is then cooled by dropping in fragments of ice, or dissolving in it powdered sal-ammoniac, until a deposition of moisture begins to make its appearance on the outside, dimming the bright metallic surface. The temperature of the dew-point is then read off upon the thermometer, and compared with that of the air.

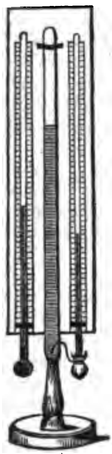
Suppose, by way of example, that the latter were 70° and the dew-point 50°; the elasticity of the watery vapor present would correspond to a maximum density proper to 50°, and would support a column of mercury ·375 inch high. If the barometer on the spot stood at 30 inches, therefore, 29·652 inches would be supported by the pressure of the dry air, and the remaining ·375 inch by the vapor. Now a cubic foot of such a mixture must be looked upon as made up of a cubic foot of dry air, and a cubic foot of watery vapor, occupying the same space, and having tensions indicated by the numbers just mentioned. A cubic foot, or 1728 cubic inches of vapor at 70° would become reduced by contraction, according to the usual law, to 1662·8 cubic inches at 50°; this vapor would be at its maximum density, having the specific gravity pointed out in the table; hence 1662·8 cubic inches would weigh 4·11 grains. The weight of the aqueous vapor contained in a cubic foot of air will thus be ascertained. In this country the difference between the temperature of the air and the dew-point seldom reaches 30°; but in the Deccan, with a temperature of 90°, the dew-point has been seen as low as 29°, making the degree of dryness 61°.*

Another method of finding the proportion of moisture present in the air is to observe the rapidity with which evaporation takes place, and which is always in some relation to the degree of dryness. The bulb of a thermometer

* Mr. Daniell, Introduction to Chemical Philosophy, p. 154.

is covered with muslin, and kept wet with water; evaporation produces cold, as will presently be seen, and accordingly the thermometer soon sinks below the actual temperature of the air. When it comes to rest, the degree is noticed, and from a comparison of the two temperatures an approximation to the dew point can be obtained by the aid of a mathematical formula contrived for the purpose. This is called the wet-bulb hygrometer; it is often made in the manner shown in the margin, where one thermometer serves to indicate the temperature of the air, and the other to show the rate of evaporation, being kept wet by the little water reservoir.

Fig. 36.



It will be apparent, from what has been already said, that the circumstances most favorable to the condensation of a vapor occur when cold and pressure are conjoined. The perfect resemblance in every respect which vapors bear to permanent gases led, very naturally, to the idea that the latter might, by the application of suitable means, be made to assume the liquid condition; and this surmise has, in the hands of Mr. Faraday, been to a great extent verified. It has been shown that out of the small number of such substances, not less than eight gave way; and it is quite fair to infer that had means of sufficient power been at hand, the rest would have shared the same fate, and proved to be nothing more than the vapors of volatile liquids in a state very far removed from that of their maximum density. The subjoined table represents Mr. Faraday's results, with the pressure in atmospheres, and the temperature at which the condensation took place.*

	Atmospheres.	Temp.
Sulphurous acid	2	45°
Sulphuretted hydrogen	17	50
Carbonic acid	36	32
Chlorine	4	60
Nitrous oxide	50	45
Cyanogen	3·6	45
Ammonia	6·5	50
Hydrochloric acid	40	50

The method of proceeding was very simple; the materials were sealed up in a strong narrow tube, together with a little pressure-guage, consisting of a slender tube closed at one end, and having within it, near the open extremity, a globule of mercury. The gas being disengaged by the application of heat,

Fig. 37.

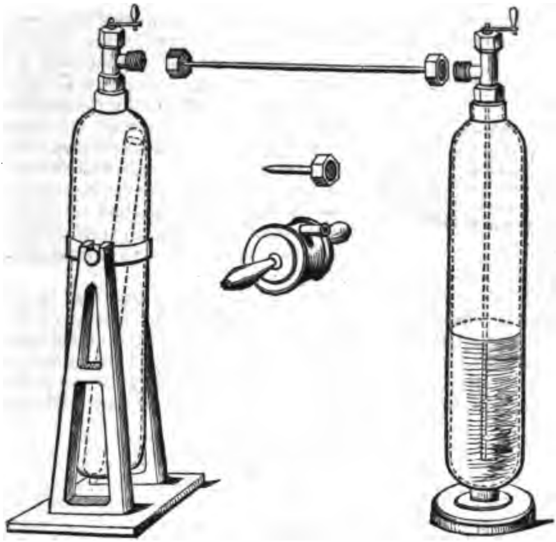
or otherwise, accumulated in the tube, and by its own pressure brought about condensation. The force required for this purpose was judged of by the diminution of volume of the air in the guage.

Since these beautiful experiments were made, means have been devised for obtaining liquefied carbonic acid in much larger quantity; Sir Isambard Brunel, and, more recently, M. Thilorier, of Paris, succeeded in obtaining this

* Phil. Trans. for 1823, p. 189.

curious liquid in great abundance. The apparatus of M. Thilorier consists of a pair of extremely strong metallic vessels, one of which is destined to serve the purpose of a retort, and the other that of a receiver. They are made either of thick cast-iron or gun-metal, or, still better, of the best and heaviest boiler-plate, and are furnished with stop-cocks of a particular kind, the workmanship of which must be excellent. The generating vessel or retort has a pair of trunnions upon which it swings in an iron frame. The joints are secured by collars of lead, and every precaution taken to prevent leakage under the enormous pressure the vessel has to bear. The receiver resembles the retort in every respect; it has a similar stop-cock, and is connected with the retort by a strong copper tube and a pair of union screw-joints; a tube passes from the stop-cock downwards, and terminates near the bottom of the vessel.

Fig. 38.



The operation is thus conducted: 2¾ lbs. of bicarbonate of soda, and 6½ lbs. of water at 100°, are introduced into the generator; oil of vitriol, to the amount of 1½ lb. is poured into a copper cylindrical vessel, which is lowered down into the mixture, and set upright; the stop-cock is then screwed into its place, and forced home by a spanner and mallet. The machine is next tilted up on its trunnions, that the acid may run out of the cylinder and mix with the other contents of the generator; and this mixture is favored by swinging the whole backwards and forwards for a few minutes, after which it may be suffered to remain a little time at rest.

The receiver, surrounded with ice, is next connected to the generator, and both cocks opened; the liquefied carbonic acid distils over into the colder vessel, and there again in part condenses. The cocks are now closed, the vessels disconnected, the cock of the generator opened to allow the contained gas to escape; and lastly, when the issue of gas *has quite ceased*, the stop-cock itself

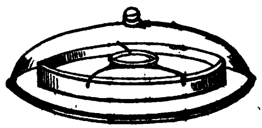
unscrewed, and the sulphate of soda turned out. This operation must be repeated five or six times before any very considerable quantity of liquefied acid will have accumulated in the receiver. When the receiver thus charged has its stop-cock opened, a stream of the liquid is forcibly driven up the tube by the elasticity of the gas contained in the upper part of the vessel.

It will be quite proper to point out to the experimenter the great personal danger he incurs in using this apparatus unless the greatest care be taken in its management. A dreadful accident has already occurred in Paris by the bursting of one of the iron vessels.

The cold produced by evaporation has been already adverted to; it is simply an effect arising from the conversion of sensible heat into latent by the rising vapor, and it may be illustrated in a variety of ways. A little ether dropped on the hand thus produces the sensation of great cold, and water contained in a thin glass tube, surrounded by a bit of rag, is speedily frozen when kept wetted with ether.

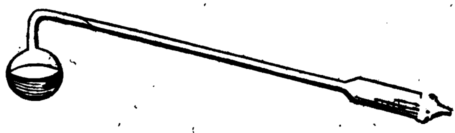
When a little water is put into a watch-glass, supported by a triangle of wire over a shallow glass dish of sulphuric acid placed on the plate of a good air-pump, the whole covered with a low receiver, and the air withdrawn as perfectly as possible, the water is in a few minutes converted into a solid mass of ice, and the watch-glass very frequently broken by the expansive power of the lower portion, a thick crust first forming on the surface. The absence of the impediment of the air, and the rapid absorption of watery vapor by the oil of vitriol, induce such quick evaporation, that the water has its temperature almost immediately reduced to the freezing point.

Fig. 39.



The same fact is shown by a beautiful instrument contrived by Dr. Wollaston, called a *cryophorus* or frost-carrier. It is made of glass, of the figure represented, and contains a small quantity of water, the rest of the space being vacuous. When all the water is turned into the bulb, and the empty extremity plunged into a mixture of ice and salt, the solidification of the vapor gives rise to such a quick evaporation from the surface of the water, that the latter freezes.

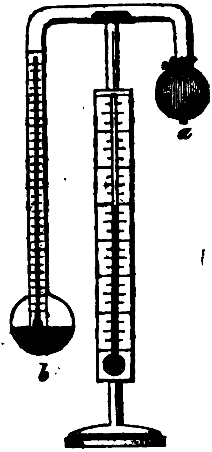
Fig. 40.



All means of producing artificial cold yield, however, to that derived from the evaporation of the liquefied carbonic acid, just mentioned. When a jet of that liquid is allowed to issue into the air from a narrow aperture, such an intense degree of cold is produced by the vaporization of a part, that the remainder freezes to a solid, and falls in a shower of snow. By suffering this jet of liquid to flow into a metal box provided for the purpose, shown in the drawing of the apparatus, a large quantity of the solid acid may be obtained: it closely resembles snow in appearance, and when held in the hand occasions a painful sensation of cold, while it gradually disappears. Mixed with a little ether, which seems to dissolve it, and poured upon a mass of mercury, the latter is almost instantly frozen, and in this way pounds of the solidified metal may be obtained.

The principle of the cryophorus has been very happily applied by Mr. Daniell to the construction of a dew-point hygrometer. The instrument itself is figured in the margin. It consists of a bent glass tube terminated by two bulbs, one of which *b*, is half filled with ether, the whole being vacuous, as respects atmospheric air. A delicate thermometer is contained in the longer limb, the bulb of which dips into the ether; a second thermometer on the stand serves to show the actual temperature of the air. The upper bulb *a*, is covered with a bit of muslin. When an observation is to be made, the liquid is all transferred to the lower bulb, and ether dropped upon the upper one, until by the cooling effects of evaporation a distillation of the contained liquid takes place from one part of the apparatus to the other, by which such a reduction of temperature of the ether is brought about, that dew is deposited on the outside of the bulb *b*, which is made of black glass in order that it may be more easily seen. The difference of temperature indicated by the two thermometers is then read off.

Fig. 41.



CAPACITY FOR HEAT; SPECIFIC HEAT.

Let the reader renew a supposition made when the doctrine of latent heat was under consideration; let him imagine the existence of a uniform source of heat, and its intensity such as to raise one pound of water 10° in 30 minutes. If, now, the experiment be repeated with equal weights of mercury and oil, it will be found, that instead of 30 minutes, 1 minute will suffice in the former case, and 15 minutes in the latter.

This experiment serves to point out the very important fact, that different bodies have different *capacities for heat;* that equal weights of water, oil, and mercury require, in order to rise through the same range of temperature, quantities of heat in the proportion of the numbers 30, 15, and 1. This is often expressed by saying that the *specific heat* of water is 30 times as great as that of mercury, and the specific heat of oil 15 times as great.

Again, if equal weights of water at 100°, and oil at 40°, be agitated together, the temperature of the whole will be found to be 80°, instead of 70°, the mean of the two; and if the temperature be reversed, that of the mixture will be only 60°. Thus,

$$\left.\begin{array}{l}\text{1 lb. water at } 100^\circ \\ \text{1 lb. of oil at } 40\end{array}\right\}\text{ give a mixture at } 80^\circ\text{; hence,}$$

Loss by the water, 20°.
Gain by the oil, 40°.

$$\left.\begin{array}{l}\text{1 lb. of water at } 40 \\ \text{1 lb. of oil at } 100\end{array}\right\}\text{ give a mixture at } 60^\circ\text{; hence,}$$

Gain of water, 20°.
Loss of oil, 40°.

This shows the same fact, that water requires twice as much heat as oil to produce the same thermometric effect.

There are three distinct methods by which the specific heat of various substances may be estimated. The first of these is by observing the quantity of ice melted by a given weight of the substance heated to a particular tempe-

rature; the second is by noting the time which the heated body requires to cool down through a certain number of degrees; and the third, is the method of mixture, on the principle illustrated; this latter method is preferred as the most accurate.

The determination of the specific heat of different substances has occupied the attention of many experimenters; among these MM. Dulong and Petit, and recently, M. Regnault, deserve especial mention. It appears that each solid and liquid has its own specific heat; and it is probable that this, instead of being a constant quantity, varies with the temperature. Very little is known respecting the specific heat of gases; the investigation being attended with the greatest difficulties; one thing, however, is clear, namely, that the specific heat varies with the state of condensation, being greater in proportion to the rarefaction of the gas. Thus, when air is expanded, a fall of temperature results, and when it is compressed, heat is evolved, which may even reach the temperature of ignition; syringes by which tinder is kindled are constructed on this principle. In the upper regions of the atmosphere the cold is intense; snow covers the highest mountain-tops even within the tropics, and this is due to increased capacity for heat of the expanded air. MM. Dulong and Petit observed in the course of their investigation a most remarkable circumstance. If the specific heats of bodies be computed upon equal weights, numbers are obtained, all different, and exhibiting no relations among themselves; but if, instead of equal weights, quantities be taken in the proportion of the chemical equivalents, an almost perfect coincidence in the numbers will be observed, showing that some exceedingly intimate connection must exist between the relations of bodies to heat and their chemical nature; and when the circumstance is taken into view that relations of even a still closer kind link together chemical and electrical phenomena, it is not too much to expect that ere long some law may be discovered far more general than any with which we are yet acquainted.

The following table is extracted from the memoirs of M. Regnault, with whose results most of the experiments of Dulong and Petit closely coincide.

Substances.	Specific heat of equal weights.	Specific heat of equivalent weights.
Water	1·00000	
Oil of Turpentine	·42593	
Glass	·19768	
Iron	·11379	3·0928
Zinc	·09555	3·0872
Copper	·09515	3·0172
Lead	·03140	3·2581
Tin	·05623	3·3121
Nickel	·10863	3·2176
Cobalt	·10696	3·1628
Platinum	·03243	3·2054
Sulphur	·20259	3·2657
Mercury	·03332	3·7128
Silver	·05701	6·1742
Arsenic	·08140	6·1326
Antimony	·05077	6·5615
Gold	·03244	6·4623
Iodine	·05412	6·8462
Bismuth	·03084	2·1917

Of the numbers in the second column, the first ten approximate far too closely to each other to be the result of mere accidental coincidence; the five that follow are very nearly twice as great; and the last is one-third less.

Independently of experimental errors, there are many circumstances which tend to show, that if all modifying causes could be compensated, or their effects allowed for, the law would be rigorously true.

The observations thus made upon elementary substances have been extended by M. Regnault to a long series of compounds, and the same curious law found, with the above limitations, to prevail throughout, save in a few isolated cases, of which an explanation can perhaps be given.

Except in the case of certain metallic alloys, where the specific heats were the mean of those of their constituent metals, no obvious relation can be traced between the specific heat of the compound body, and of its components. The most general expression of the facts that can be given is the following:—

In bodies of similar chemical constitution, the specific heats are in an inverse ratio to the equivalent weights, or to a multiple or submultiple of the latter.— Simple as well as compound bodies will be comprehended in this law.*

Sources of Heat.—The first and greatest, and compared with which all others are totally insignificant, is the sun. The luminous rays are accompanied by rays of a heating nature, which, striking against the surface of the earth, elevate its temperature; this heat is communicated to the air by convection, as already described; air and gases in general not being sensibly heated by the passage of the rays.

A second source of heat is supposed to exist in the interior of the earth. It has been observed, that in sinking mine-shafts, boring for water, &c., the temperature rises in descending at the rate, it is said, of about 1° for every 45 feet, or 117° per mile. On the supposition that the rise continued at the same rate, at the depth of less than two miles, the earth would have the temperature of boiling water; at nine miles it would be red-hot; and at 30 or 40 miles depth, all known substances would be in a state of fusion.†

According to this idea, the earth must be looked upon as an intensely-heated, fluid spheroid, covered with a crust of solid badly-conducting matter, cooled by radiation into space, and bearing somewhat the same proportion in thickness to the ignited liquid within, that the shell of an egg does to its fluid contents. Without venturing to offer any opinion on this theory, it may be sufficient to observe that it is not positively at variance with any known fact; that the figure of the earth is really such as would be assumed by a fluid mass; and lastly, that it offers the best explanation we have of the phenomena of hot springs and volcanic eruptions, and agrees with the chemical nature of their products.

The smaller, and what may be called secondary, sources of heat, are very numerous; they may be divided, for the present, into two groups, mechanical motion and chemical combination. To the first, must be referred elevation of temperature by friction and blows; and to the second, the effects of combustion and animal respiration. With regard to the heat developed by friction, it appears to be indefinite in amount, and principally dependent upon the nature of the rubbing surfaces. An experiment of Count Rumford is on record, in which the heat developed by the boring of a brass cannon, was sufficient to bring to the boiling-point two and a half gallons of water, while the dust or shavings of metal, cut by the borer, weighed a few ounces only. Sir H. Davy melted two pieces of ice by rubbing them together in vacuo at 32°; and uncivilized men, in various parts of the world, have long been known to obtain fire by rubbing together two pieces of dry wood. The origin of the heat in these cases is by no means intelligible.

* Ann. Chim. et Phys., lxxiii. p. 5; and the same, 3d Series, i. p. 129.

† The new artesian well at Grenelle, near Paris, has a depth of 1794-5 English feet; it is bored through the chalk basin to the sand beneath; the work occupied seven years and two months. The temperature of the water, which is exceedingly abundant, is 82° Faht.; the mean temperature of Paris is 51° Faht.; the difference is 31°, which gives a rate of about 1° for 58 feet.

LIGHT.

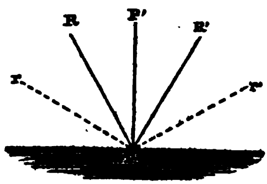
The subject of light is so little connected with elementary chemistry, that a very slight notice of some of the most important points will suffice.

Two views have been entertained respecting the nature of light. Sir Isaac Newton imagined that luminous bodies emitted, or shot out, infinitely small particles in straight lines, which, by penetrating the transparent part of the eye, and falling upon the nervous tissue, produced vision. Other philosophers drew a parallel between the properties of light and those of sound, and considered that as sound is certainly the effect of undulations, or little waves, propagated through elastic bodies in all directions, so light might be nothing more than the consequence of similar undulations, transmitted with inconceivable velocity through a highly elastic medium, of excessive tenuity, filling all space, and occupying the intervals between the particles of material substances, to which they gave the name of *ether*. The wave-hypothesis of light is at present most in favor, as it serves to explain certain singular phenomena, discovered since the time of Newton, with greater facility than the other.

A ray of light emitted from a luminous body proceeds in a straight line, and with extreme velocity. Certain astronomical observations afford the means of approximating to a knowledge of this velocity. The satellites of Jupiter revolve about the planet in the same manner as the moon about the earth, and the time required by each for the purpose is exactly known. Now, it has been found by accurate observation, that when the earth is at its greatest distance from Jupiter, the passage of any particular satellite into the shadow of the planet takes place 16 minutes and 26 seconds later than when the earth is at the opposite point of its orbit;—that is, in other words, that the ray of light from the satellite requires that interval of time to pass across the orbit of the earth, and since this space is little short of 200 millions of miles, the velocity of light cannot be less than 200,000 miles in a second of time. It will be seen, hereafter, that this rapidity of transmission is rivaled by that of the electrical agent.

When a ray of light falls on a plane surface, it may be disposed of in three ways; it may be absorbed and disappear altogether; it may be reflected, or thrown off, according to a particular law; or it may be partly absorbed, partly reflected, and partly transmitted. The first happens when the surface is perfectly black and destitute of lustre; the second, when a polished surface of any kind is employed; and the third, when the body upon which the light falls is of the kind called transparent, as glass or water.

Fig. 42.



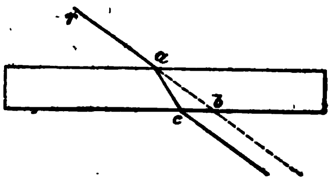
The law of reflection is extremely simple. If a line be drawn perpendicular to the surface upon which the ray falls, and the angle contained between the ray and the perpendicular measured, it will be found that the ray, after reflexion, takes such a course as to make with the perpendicular an equal angle on the opposite side of the latter. A ray of light, R, falling at the point P, will be reflected in the direction PR′, making the angle R′PP′ equal to the angle RPP′; or a ray from the

point r falling upon the same spot will be reflected to r' in virtue of the same law. Further, it is to be observed, that the incident and reflected rays are always contained in the same vertical plane.

The same rule holds good if the mirror be curved as a portion of a sphere, the curve being considered as made up of a multitude of little planes. Parallel rays become permanently altered in direction when reflected from curved surfaces, becoming divergent or convergent according to the kind of curvature.

It has just been stated that light passes in straight lines; but this is only true so long as the medium through which it travels preserves the same density and the same chemical nature; when this ceases to be the case, the ray of light is bent from its course into a new one, or, in optical language, is said to be *refracted*.

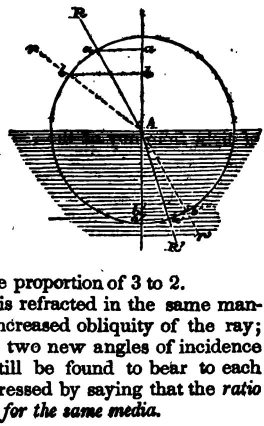
Fig. 43.



Let r be a ray of light falling upon a plate of some transparent substance with parallel sides, such as a piece of thick plate glass; and a its point of contact with the upper surface. The ray, instead of holding a straight course and passing into the glass, in the direction a b, will be bent downwards to c; and on leaving the glass, and issuing into the air on the other side, it will again be bent, but in the opposite direction, so as to make it parallel to the continuation of its former track. The general law is thus expressed:—When the ray passes from a rare to a denser medium, it is refracted *towards* a line perpendicular to the surface of the latter; and conversely, when it leaves a dense medium for a rarer one, it is refracted *from* a line perpendicular to the surface of the denser substance; in the former case the angle of incidence is said to be greater than that of refraction; in the latter it is said to be less.

The amount of refraction, for the same medium, varies with the obliquity with which the ray strikes the surface. When perpendicular to the latter, it passes without change of direction at all, and in other positions, the refraction increases with the obliquity.

Fig. 44.



Let R represent a ray of light falling upon the surface of a mass of plate glass at the point A. From this point let a perpendicular be raised and continued into the new medium, and around the same point, as a centre, let a circle be drawn. According to the law just stated, the refraction must be towards the perpendicular; in the direction AR′ for example. If the length of the radius be taken for unity, the number expressing the length of the line a a is what is called the sine of the angle of incidence, and the number expressing the length of line a' a', the sine of the angle of refraction; let these two lines be compared; their length will be, in the case supposed, in the proportion of 3 to 2.

Now let another ray be taken, such as r; it is refracted in the same manner to r', the bending being greater from the increased obliquity of the ray; but what is very remarkable, if the sines of the two new angles of incidence and refraction be again compared, they will still be found to bear to each other the proportion of 3 to 2. The fact is expressed by saying that the *ratio of the sines of incidence and refraction is constant for the same media.*

The plane of refraction coincides moreover with that of incidence.

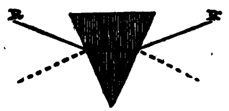
Different bodies possess different refractive powers; generally speaking, the densest substances refract most. Combustible bodies have been noticed to possess greater refractive power than their density would indicate, and from this observation Sir I. Newton predicted the combustible nature of the diamond long before anything was known respecting its chemical composition.

The method adopted for describing the comparative refractive powers of different bodies is to state the ratio borne by the sine of the angle of refraction to that of incidence, making the former unity;—this is called the *index of refraction* for the substance. Thus, in the case of glass, the index of refraction will be 1·5. When this is once known for any particular transparent body, the effect of the latter upon a ray of light entering it, in any position, can be calculated by the aid of the law of sines.

Substances.	Index of refraction.	Substances.	Index of refraction.
Tabasheer*	1·10	Garnet	1·80
Ice	1·30	Glass, with much oxide of lead	1·90
Water	1·34	Zircoon	2·00
Fluor spar	1·40	Phosphorus	2·20
Plate glass	1·50	Diamond	2·50
Rock crystal	1·60	Chromate of lead	3·00
Chrysolite	1·69		
Sulphuret of Carbon	1·70		

When a luminous ray enters a mass of substance differing in refractive power from the air, and whose surfaces are not parallel, it becomes permanently deflected from its course and altered in its direction. It is upon this principle that the properties of prisms and lenses depend. To take an example.—Let the sketch represent a triangular prism of glass, upon the side of which the ray of light R may be supposed to fall. This ray will of course be refracted in entering the glass towards a line perpendicular to the first surface, and again, from a line perpendicular to the second surface on emerging into the air. The result will be a total change in the direction of the ray.

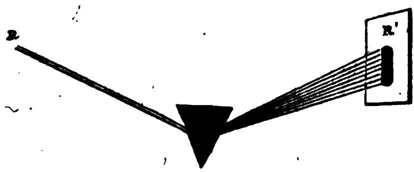
Fig. 45.



A convex lens is thus enabled to converge rays of light falling upon it, and a concave lens to separate them more widely; each separate part of the surface of the lens producing its own independent effect.

The light of the sun and celestial bodies in general, as well as that of the electric spark, and of all ordinary flames, is of a compound nature. If a ray of light from any of the sources mentioned be admitted into a dark room by

Fig. 46.

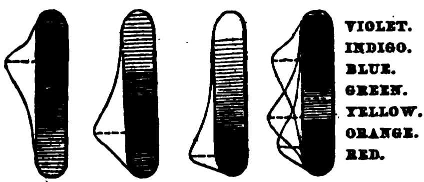


* A siliceous deposit in the joints of the bamboo.

a small hole in a shutter, or otherwise, and suffered to fall upon a glass prism in the manner described above, it will not only be refracted from its straight course, but will be decomposed into a number of colored rays, which may be received upon a white screen placed behind the prism. When solar light is employed the colors are extremely brilliant, and spread into an oblong space of considerable length. The upper part of this image or *spectrum* will be violet, and the lower red, the intermediate portion, commencing from the violet, being indigo, blue, green, yellow, and orange, all graduating imperceptibly into each other. This is the celebrated experiment of Sir I. Newton, and from it he drew the inference that white light is composed of seven primitive colors, the rays of which are differently refrangible by the same medium, and hence, capable of being thus separated. The violet rays are most refrangible, and the red rays least.

Sir D. Brewster is disposed to think that out of Newton's seven primitive colors, four are really compound, and formed by the superposition of the three remaining, namely, blue, yellow, and red, which alone deserve the name of primitive. When these three kinds of rays are mixed, or superimposed, in a certain definite manner, they produce white light, but when one or two of them are in excess, then an effect of color is perceptible simple in the first case and compound in the second. There are rays of all refrangibilities of each color, and consequently white light in every part of the spectrum, but then they are unequally distributed; the blue rays are more numerous near the top, the yellow towards the middle, and the red at the bottom, the excess of each color producing its characteristic effect. In the diagram below the intensity of each color is represented by the height of a curve, and the effects of mixture will be intelligible by a little consideration.

Fig. 47.



Bodies of the same mean refractive power do not always equally disperse or spread out the differently colored rays; because the principal yellow or red rays, for instance, are equally refracted by two prisms of different materials, it does not follow that the blue or the violet shall be similarly affected. Hence, prisms of different varieties of glass, or other transparent substances, give, under similar circumstances, very different spectra, both as respects the length of the image, and the relative extent of the colored bands.

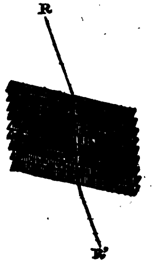
The colors of natural objects are supposed to result from the power which the surfaces of the bodies possess of absorbing some of the colored rays, while they reflect or transmit, as the case may be, the remainder. Thus, an object appears red because it absorbs, or causes to disappear, a portion of the yellow and blue rays composing the white light by which it is illuminated.

A ray of common light made to pass through certain crystals of a particular order is found to undergo a very remarkable change. It becomes split or divided into two rays, one of which follows the general law of refraction, and

the other takes a new and extraordinary course, dependent on the position of the crystal. This effect, which is called double refraction, is beautifully illustrated in the case of Iceland spar, or crystallized carbonate of lime. On placing a rhomb of this substance on a piece of white paper, on which a mark or line has been made, the object will be seen doubled.

Again, if a ray of light be suffered to fall upon a plate of glass at an angle of 56° 45′, the portion of the ray which suffers reflexion will be found to have acquired properties which it did not before possess, for, on throwing it under the same angle upon a second glass plate, it will be observed that there are two particular positions of the latter in which the ray ceases to be reflected. Light which has suffered this change is said to be *polarized*.

Fig. 48.



The light which passes through the first, or polarizing plate is also to a certain extent in this peculiar condition, and by employing a series of similar plates, held parallel to the first, this effect may be greatly increased; a bundle of 15 or 20 such plates may be used with great convenience for the experiment. It is to be remarked, also, that the light polarized by transmission in this manner is in an opposite state to that polarized by reflexion; that is when examined by a second or *analyzing* plate held at the angle before-mentioned, it will be seen to be reflected when the other disappears, and to be absorbed when the first is reflected.

It is not every substance which is capable of polarizing light in this manner; glass, water, and certain other bodies bring about the change in question, each having a particular polarizing angle at which the effect is greatest. Polished metals, on the contrary, do not exhibit these phenomena, at least in the same manner. The two rays into which a pencil of common light divides itself in passing through a doubly refracting crystal are found on examination to be polarized in a very complete manner, and also transversely, the one being capable of reflexion when the other vanishes. With a rhomb of transparent Iceland spar of tolerably large dimensions the two oppositely polarized rays may be widely separated and examined apart.

There is yet another method of polarization, by the employment of plates of the mineral tourmaline cut parallel to the axis of the crystal. This body polarizes by simple transmission, the ray falling perpendicular to its surface; a part of the light is absorbed, and the remainder modified in the manner described. When two such plates are held with their axes parallel, as in fig. 49, light traverses them both freely, but when one of them is turned round in

Fig. 49.

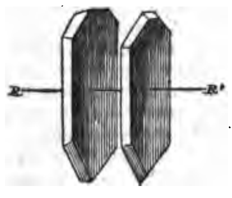
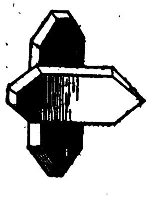


Fig. 50.



the manner shown in the second cut, so as to make the axis cross at right angles, the light is almost wholly stopped, if the tourmalines be good. A

plate of the mineral thus becomes an excellent test for discriminating between polarized light and that which has not undergone the change.

Some of the most splendid phenomena of the science of light are exhibited when thin plates of doubly refracting substances are interposed between the polarizing arrangement and the analyzer.

The luminous rays of the sun are accompanied, as already mentioned, by others which possess heating powers. If the temperature of the different colored spaces in the spectrum be tried with a delicate thermometer, it will be found to increase from the violet to the red extremity, and when the prism is of some particular kinds of glass, the greatest effect will be manifest a little beyond the visible red ray. It is inferred from this that the heating rays are among the least refrangible components of the solar beam.

Again, it has long been known that chemical changes both of combination and of decomposition, but more particularly the latter, could be effected by the action of light. Chlorine and hydrogen combine at common temperatures only under the influence of light, and parallel cases occur in great numbers in organic chemistry; the blackening and decomposition of salts of silver are familiar instances of the chemical powers of the same agent. Now it is not the luminous part of the ray which effects these changes; they are produced by certain invisible rays accompanying the others, and which are found most abundantly in and beyond the violet part of the spectrum. It is there that the chemical effects are most marked, although the intensity of the light is exceedingly feeble. The chemical rays are thus directly opposed to the heating rays in the common spectrum in their degree of refrangibility, since they exceed all the others in this respect.

In the year 1802,* Mr. Thomas Wedgwood proposed a method of copying paintings on glass by placing behind them white paper or leather moistened with solution of nitrate of silver, which became decomposed and blackened by the transmitted light in proportion to the intensity of the latter, and Davy, in repeating these experiments, found that he could thus obtain tolerably accurate representations of objects of a texture partly opaque and partly transparent, such as leaves and the wings of insects, and even copy, with a certain degree of success, the images of small objects obtained by the solar microscope. These pictures, however, required to be kept in the dark, and only examined by candle-light, otherwise they became obliterated by the blackening of the whole surface from which the salt of silver could not be removed. These attempts at light-painting attracted but little notice till the publication of Mr. Fox Talbot's† papers read before the Royal Society, in January and February, 1839, in which he detailed two methods of fixing the pictures produced by the action of light on paper impregnated with chloride of silver, and at the same time described a plan by which the sensibility of the prepared paper may be increased to the extent required for receiving impressions from the images of the camera obscura.

Very shortly afterwards, Sir John Herschell‡ proposed to employ solutions of the alkaline hyposulphites for removing the excess of chloride of silver from the paper, and thus preventing the further action of light, and this plan has been found exceedingly successful. The greatest improvement, however, which the curious art of photogenic drawing has received, is due to Mr. Talbot,§ who, in a more recent communication to the Royal Society, described a method by which paper of such sensibility could be prepared as to permit its application to the taking of portraits of living persons by the aid of a good

* Journal of the Royal Institution, i. p. 170.
† Phil. Mag., March, 1839.
‡ Phil. Trans. for 1840, p. 1.
§ Phil. Mag., August, 1841.

camera obscura, the time required for a perfect impression never exceeding a few minutes. The portraits executed in this manner by Mr. Collen are beautiful in the highest degree, and leave little room for improvement in any respect. The process itself is rather complex, and demands a great number of minute precautions, only to be learned by experience, but which are indispensable to perfect success. The general plan is the following:—

Writing-paper of good quality is washed on one side with a moderately dilute solution of nitrate of silver, and left to dry spontaneously in a dark room; when dry it is dipped into a solution of iodide of potassium and again dried. These operations should be performed by candle-light. When required for use, the paper thus coated with yellow iodide of silver is brushed over with a solution containing nitrate of silver, acetic acid, and gallic acid, and once more carefully dried by gentle warmth. This *kalotype* paper is so sensitive that exposure to diffuse day-light for one second suffices to make impression upon it, and even the light of the moon produces the same effect, although a much longer time is required.

The images of the camera obscura are at first invisible, but are made to appear in full intensity by once more washing the paper with the above-mentioned mixture and warming it before the fire, when the blackening effect commences and reaches its maximum in a few minutes.

The picture is of course *negative*, the lights and shadows being reversed; to obtain *positive* copies nothing more is necessary than to place a piece of ordinary photographic paper prepared with chloride of silver beneath the kalotype impression, cover them with a glass plate, and expose the whole to the light of the sun for a short time.

Before this can be done, the kalotype must, however, be fixed, otherwise it will blacken, and this is effected by immersion in a solution of bromide of potassium, and well washing with water.

Sir John Herschell has shown that a great number of other substances can be employed in these photographic processes by taking advantage of the singular de-oxidizing effects of certain portions of the solar rays. Paper washed with a solution of a peroxide salt of iron becomes capable of receiving impressions of this kind, which may afterwards be made evident by red ferrocyanide of potassium, or chloride of gold. Vegetable colors are also acted upon in a very curious and apparently definite manner by the different parts of the spectrum.*

The Daguerreotype is another remarkable instance of the decomposing effects of the solar rays. A clean and highly-polished plate of silvered copper is exposed for a certain period to the vapor of iodine, and then transported to the camera obscura. In the most improved state of the process, a very short time suffices for effecting the necessary change in the film of iodide of silver. The picture, however, only becomes visible by exposing it to the vapor of mercury, which attaches itself in the form of exceedingly minute globules to those parts which have been most acted upon, that is to say, to the lights, the shadows being formed by the dark polish of the metallic plate. Lastly, the drawing is washed with a solution of hyposulphite of soda to remove the undecomposed iodide of silver, and render it permanent.

The images of objects thus produced bear the most minute examination with a magnifying glass, the smallest details being depicted with perfect fidelity.

The most extraordinary discovery of all is, perhaps, that recently made by Professor Moser,† that bodies of all kinds separated by a very small interval seem mutually to impress their images on each other, which become manifest

* Phil. Trans., 1842, p. 1.
† See Liebig's Annalen, xliv. p. 173.

when the surfaces are breathed upon or exposed to any easily condensible vapor. This effect is quite independent of light, and takes place in perfect darkness. An engraving, for example, placed behind a plate of glass in the usual manner, and left for many years, will often be found to have impressed upon the latter an outline of its principal features, rendered distinctly visible by the unequal deposition of the film of minute dust which gradually collects upon glass surfaces. These matters well deserve careful study, and may possibly lead to some important generalizations.

With the aid of this slight notice of optical science, the subject of Heat may be resumed and completed.

RADIATION, REFLEXION, ABSORPTION, AND TRANSMISSION OF HEAT.

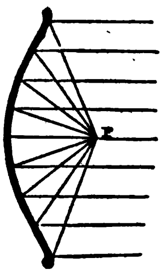
RADIATION OF HEAT.

If a red-hot ball be placed upon a metallic support and left to itself, cooling immediately commences, and only stops when the temperature of the ball is reduced to that of the surrounding air. This effect takes place in three ways: heat is conducted away from the ball through the substance of the support; another portion is removed by the convective power of the air; and the residue is thrown off from the heated body in straight lines or rays, which pass through air without interruption, and become absorbed by the surfaces of neighboring objects which happen to be presented to their impact.

This radiant or radiated heat resembles, in very many respects, ordinary light; it suffers reflection from polished surfaces according to the same law; it is absorbed by those that are dull or rough; it moves with extreme velocity; and, finally, it traverses certain transparent media, undergoing refraction at the same time, in obedience to the laws which regulate that phenomenon in optics.

The fact of the *reflexion* of heat may be very easily proved. If a person stand before a fire in such a position that his face may be screened by the mantel-shelf, and if he then take a bright piece of metal, as a sheet of tinned plate, and hold it in such a manner that the fire may be seen by reflexion, at the same moment a distinct sensation of heat will be felt.

Fig. 51.



The apparatus best fitted for studying these facts consists of a pair of concave metallic mirrors of the form called parabolic. The parabola is a curve possessing very peculiar properties, one of the most prominent being the following: A tangent drawn to any part of the curve, makes equal angles with two lines, one of which proceeds from the point where the tangent touches the curve in a direction parallel to what is called the axis of the parabola, and the other from the same spot through a point in front of the curve called the focus. It results from this, that parallel rays either of light or heat, falling upon a mirror of this particular curvature in a direction parallel to the axis of the parabola, will be all reflected to a single point at the focus; and rays diverging from this focus and impinging upon the mirror, will, after reflexion, become parallel.

If two such mirrors be placed opposite to each other at a considerable distance, and so adjusted that their axes shall be coincident, and a hot body placed in the focus of the one, while a thermometer occupies that of the other, the reflexion of the rays of heat will become manifest by their effect upon the instrument. In this manner, with a pair of by no means very perfect mirrors, 18 inches in diameter, separated by an interval of 20 feet or more, amadou or gunpowder may be readily fired by a red-hot ball in the focus of the opposite mirror.

Fig. 52.

The power of radiation varies exceedingly with different bodies, as may be easily proved. If two similar vessels of equal capacity be constructed of thin metal, and the surface of one highly polished, while that of the other is covered with lamp-black, and both filled with hot water of the same temperature, and their rate of cooling observed from time to time with a thermometer, it will be constantly found that the blackened vessel loses heat much faster than the one with bright surfaces; and since both are put on a footing of equality in other respects, this difference, which will often amount to many degrees, must be ascribed to the superior emissive power of the film of soot.

By another arrangement, a numerical comparison can be made of these differences. A cubical metallic vessel is prepared, each of whose sides is in a different condition, one being polished, another rough, a third covered with lamp-black, &c. This vessel is filled with water kept constantly at 212°, by a small steam-pipe. Each of its sides is then presented in succession to a good parabolic mirror, having in its focus one of the bulbs of the differential thermometer before described, the bulb itself being blackened. The effect produced on this instrument is taken as a measure of the comparative radiating powers of the different bodies. The late Sir John Leslie obtained by this method of experiment the following results:—

	Emissive power.		Emissive power.
Lamp-black	100	Tarnished lead	45
Writing-paper	98	Clean lead	19 *
Glass	90	Polished iron	15
Plumbago	75	Polished silver	12

The best reflecting surfaces are always the worst radiators; polished metal reflects nearly all the heat that falls upon it, while its radiating power is the feeblest of any substance tried, and lamp-black, which reflects nothing, radiates most perfectly.

The power of *absorbing* heat is in direct proportion to the power of emission. The polished metal mirror in the experiment with the red-hot ball remains quite cold, although only a few inches from the latter; or again, if a piece of gold leaf be laid upon paper, and a heated iron held over it until the paper is completely scorched, it will be found that the film of metal has perfectly defended that portion beneath it.

* The formerly supposed influence of mere difference of surface has been called in question by M. Melloni, who attributes to other causes the effects observed by Sir John Leslie, and others, among which superficial oxidation and differences of physical condition with respect to hardness and density, are among the most important. With metals not subject to tarnish, scratching the surface *increases* the emissive power when the plates have been rolled or hammered, *i. e.*, are in a compressed state, and diminishes it, on the contrary, when the metal has been cast and carefully polished without burnishing. In the case of ivory, marble, and jet, where compression cannot take place, no difference is perceptible in the radiating power of polished and rough surfaces.—Ann. Chim. et. Phys., lxx. p. 435.

The faculty of absorption seems to be a good deal influenced by color; Dr. Franklin found that when pieces of cloth of various colors were placed on snow exposed to the feeble sunshine of winter, the snow beneath them became unequally melted, the effect being always in proportion to the depth of the color; and Dr. Stark has since obtained a similar result by a different method of experimenting.

These facts afford an explanation of two very interesting and important natural phenomena, namely, the origin of dew, and the cause of the land and sea breezes of tropical countries. While the sun remains above the horizon, the heat radiated by the surface of the earth into space is compensated by the absorption of the solar beams; but when the sun sets, and this supply ceases, while the emission of heat goes on as actively as before, the surface becomes cooled until its temperature sinks below that of the air. The air in contact with the earth of course participates in this reduction of temperature; the aqueous vapor present speedily reaches its point of maximum density, and then begins to deposit moisture, whose quantity will depend upon the proportion of vapor in the atmosphere, and on the extent to which the cooling process has been carried.

It is observed that dew is most abundant in a clear calm night succeeding a hot day; under these circumstances the quantity of vapor in the air is usually very great, and at the same time radiation proceeds with most facility. At such times a thermometer laid on the ground will, after some time, indicate a temperature of 10°, 15°, or even 20° below that of the air a few feet higher. Clouds hinder the formation of dew, by reflecting back to the earth the heat radiated from its surface, and thus preventing the necessary reduction of temperature; and the same effect is produced by a screen of the thinnest material stretched at a little height above the ground. In this manner gardeners often preserve delicate plants from destruction by the frosts of spring and autumn. The piercing cold felt just before and at sunrise, even in the height of summer, is the consequence of this refrigeration having reached its maximum.

Wind also effectually prevents the deposition of dew, by constantly renewing the air lying upon the earth before it has had its temperature sufficiently reduced to cause condensation of moisture.

Many curious experiments may be made by exposing on the ground at night, bodies which differ in their powers of radiation. If a piece of black cloth and a plate of bright metal be thus treated, the former will be found in the morning covered with dew, while the latter remains dry.

Land and sea-breezes are certain periodical winds common to most sea-coasts within the tropics, but by no means confined to those regions. It is observed, that a few hours after sunrise a breeze springs up at sea, and blows directly on shore, and that its intensity increases as the day advances, and declines and gradually expires near sunset. Shortly afterwards a wind arises in exactly the opposite direction, namely, from the land towards the sea, lasts the whole of the night, and only ceases with the reappearance of the sun.

It is easy to give an explanation of these effects. When the sun shines at once upon the surface of the earth and that of the sea, the two become unequally heated from their different absorbing power; the land becomes much the warmest. The air over the heated surface of the ground, being expanded by heat, rises, and has its place supplied by colder air flowing from the sea, producing the sea-breeze. When the sun sets, both sea and land begin to cool by radiation; the rate of cooling of the latter will, however, far exceed that of the former, and its temperature will rapidly fall. The air above becoming cooled and condensed, flows outwards in obedience to the laws of fluid pressure, and displaces the warmer air of the ocean. In this manner, by an

interchange of air between sea and land, the otherwise oppressive heat is moderated, to the great advantage of those who inhabit such localities. The land and sea-breezes extend to a small distance only from the shore, but afford, notwithstanding, essential aid to coasting navigation, since vessels on either tack enjoy a fair wind during the greater part of both day and night.

TRANSMISSION OF HEAT; DIATHERMANCY.

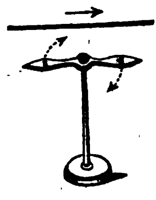
Rays of heat, in passing through air, receive no more obstruction than those of light under similar circumstances; but with other transparent media the case is different. If a parabolic mirror be taken and its axis directed towards the sun, the rays both of heat and light will be reflected to the focus, which will exhibit a temperature sufficiently high to fuse a piece of metal, or fire a combustible body. If a plate of glass be now placed between the mirror and the sun, the effect will be but little diminished.

Now, let the same experiment be made with the heat and light of a common fire; both will be concentrated by reflexion as before, but on interposing the glass, the heating effect of the focus will be reduced almost to nothing, while the light will not have undergone perceptible diminution. Thus, the rays of heat coming from the sun traverse glass with facility, which is not the case with those emanating from an ordinary red-hot body.

In the year 1833, M. Melloni published the first of a series of exceedingly valuable researches on this subject, which are to be found in detail in various volumes of the Annales de Chimie et de Physique.* It will be necessary, in the first instance, to describe the method of operations followed by this philosopher.

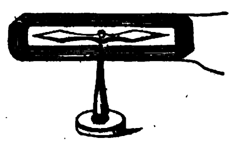
Not long before, two very remarkable facts had been discovered:—First, that a current of electricity, however produced, exercises a singular and perfectly definite action on a magnetic needle; and, secondly, that an electric current may be generated by the unequal effects of heat on different metals in contact. If a wire conveying an electrical current be brought near a magnetic needle, the latter will immediately alter its position and assume a new one, as nearly perpendicular to the wire as the mode of suspension and the magnetism of the earth will permit. When the wire, for example, is placed directly over the needle, while the current it carries travels from north to south, the needle is deflected from its ordinary direction and the north pole driven to the eastward. When the current is reversed, the same pole deviates to an equal amount towards the west. Placing the wire below the needle instead of above produces the same effect as reversing the current.

Fig. 53.



When the needle is subjected to the action of two currents in opposite directions, the one above and the other below, they will obviously concur in their effects. The same thing happens when the wire carrying the current is bent upon itself, and the needle placed between the two portions; and since every time the bending is repeated a fresh portion of the current is made to act in the same manner upon the needle, it is easy to see how a current too feeble to produce any effect when a simple straight wire is employed may be made by this contrivance to

Fig. 54.

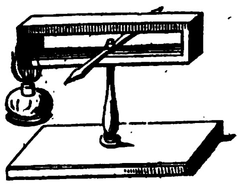


* Translated also in Taylor's Scientific Memoirs.

exhibit a powerful action on the magnet. It is on this principle that instruments called *galvanometers*, *galvanoscopes*, or *multipliers*, are constructed; they serve not only to indicate the existence of electrical currents, but to show by the effect upon the needle the direction in which they are moving. By using a very long coil of wire, and two needles immovably connected, and hung by a fine filament of silk, almost any degree of sensibility may be communicated to the apparatus.

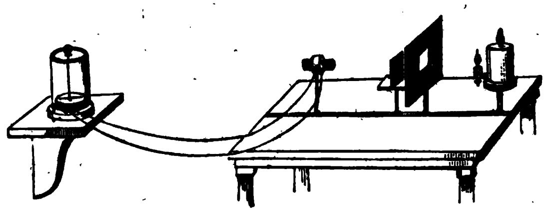
When two pieces of different metals connected together at each end have one of their joints more heated than the other, an electric current is immediately set up. Of all the metals tried, bismuth and antimony form the most powerful combination. A single pair of bars, having one of their junctions heated in the manner shown, can develop a current strong enough to deflect a compass needle placed within, and, by arranging a number in a series and heating their alternate ends, the intensity of the current may be very much increased. Such an arrangement is called a thermo-electric pile. M. Melloni constructed a very small thermo-electric pile of this kind, containing fifty-five slender bars of bismuth and antimony, laid side by side and soldered together at their alternate ends. He connected this pile with an exceedingly delicate multiplier, and found himself in the possession of an instrument for measuring small variations of temperature far surpassing in delicacy the air-thermometer in its most sensitive form, and having great advantages in other respects over that instrument when employed for the purposes to which he devoted it.

Fig. 55.



The substances whose powers of transmission were to be examined were cut into plates of a determinate thickness, and, after being well polished, arranged in succession in front of the little pile, the extremity of which was blackened to promote the absorption of the rays. A perforated screen, the area of whose aperture equaled that of the face of the pile, was placed between the source of heat and the body under trial, while a second screen served to intercept all radiation until the moment of the experiment.

Fig. 56.



After much preliminary labor for the purpose of testing the capabilities of the apparatus and the value of its indications, an extended series of researches were undertaken and carried on during a long period with great success;—some of the most curious results are given in the subjoined table.

Four different sources of heat were employed in these experiments, differing in their degrees of intensity; the naked flame of an oil-lamp; a coil of platinum wire heated to redness; blackened copper at 734°; and the same heated to 212°.

Substances. (Thickness of plate ·1 inch, nearly.)	Transmission of 100 rays of heat from			
	Oil-lamp.	Red-hot platinum.	Copper at 734°	Copper at 212°
Rock-salt, transparent and colorless	92	92	92	92
Fluor-spar, colorless	78	69	42	33
Rock-salt, muddy,	65	65	65	65
Beryl	54	23	13	0
Fluor-spar, greenish	46	38	24	20
Iceland-spar	39	28	6	0
Plate-glass	39	24	6	0
Rock-crystal	38	28	6	0
Rock-crystal, brown	37	28	6	0
Tourmaline, dark green	18	16	3	0
Citric acid, transparent	11	2	0	0
Alum, transparent	9	2	0	0
Sugar-candy	8	0	0	0
Fluor-spar, green, translucent	8	6	4	3
Ice, pure and transparent	6	0	0	0

On examining this remarkable table, which is an abstract of one much more extensive, the first thing that strikes the eye is the want of connection between the power of transmitting heat and that of transmitting light; taking for instance, the oil-lamp as the source of heat, out of a quantity of heat represented by 100 rays falling upon the pile, the proportion intercepted by similar plates of rock salt, glass and alum, may be expressed by the numbers 8, 61, and 91; and yet these bodies are equally transparent with respect to light. Generally speaking, color was found to interfere with the transmissive power, but to a very unequal extent; thus in fluor-spar, colorless, greenish, and deep green, the quantities transmitted were 78, 46, and 8, while the difference between colorless and brown rock-crystal was only 1. Bodies absolutely opaque, as wood, metals, and black marble stopped the rays completely, although it was found that the faculty of transmission was possessed to a certain extent by some which were nearly in that condition, as thick plates of brown quartz, black mica, and black glass.

When rays of heat had once passed through a plate of any substance, the interposition of a second similar plate occasioned much less loss than the first; the same thing happened when a number were interposed, the rays, after traversing one plate, being but little interrupted by others of a similar nature.

The next point to be noticed is the great difference in the properties of the rays from different sources. Out of 100 rays from each source which fell on rock-salt, the same proportion was always transmitted, whether the rays proceeded from the intensely heated flame, the red-hot platinum wire, or the copper at 734° or 212°; but this is true of no other substance in the list. In the case of plate-glass, we have the numbers 39, 24, 6, and 0, as representatives of the comparative quantities of heat transmitted through the plate from each source; or in the three varieties of fluor-spar, as below stated:—

	Flame.	Red-heat.	734°	212°
Colorless .	78	69	42	33
Greenish .	46	38	24	20
Dark green	8	6	4	3

While one substance, beryl, out of 100 rays from an intensely heated source suffers 54 to pass, and from the same number, that is, an equal quantity of heat, from metal at 212° none at all, another transmits rays from the two sources mentioned in the proportion of 8 to 3.

These, and many other curious phenomena, are fully and completely explained on the supposition, that among the invisible rays of heat differences are to be found exactly analogous to those differences between rays of light which we are accustomed to call colors. Rock-salt is the only substance yet known which is truly *diathermanous*, or equally transparent to all kinds of heat-rays; it is to the latter what white glass or water is to light; it suffers rays of every description to pass with equal facility. All other bodies act like colored glasses, absorbing certain of the rays more abundantly than the rest, and *coloring* as it were the heat which passes through them.

These heat-tints have, however, no direct relation to ordinary colors, although, no doubt, they depend, like the latter, upon peculiarities of molecular structure which are quite unknown; their existence is, nevertheless, almost as clearly made out as that of the colored rays of the spectrum. Bodies at a comparatively low temperature emit rays of such a tint only as to be transmissible by a few substances; as the temperature rises, rays of other heat colors begin to make their appearance, and transmission of some portion of these rays takes place through a greater number of bodies; while at the temperature of intense ignition, we find rays of all colors thrown out, some or other of which will certainly find their way through a great variety of substances.

By cutting rock-salt into prisms and lenses, it is easy to show that radiant heat may be refracted like ordinary light, and its beams made to converge or diverge at pleasure; and lastly, to complete the analogy, it has been shown to be susceptible of polarization by transmission through plates of doubly refracting minerals, in the same manner as light itself.*

* Dr. Forbes, Phil. Mag. for 1835; also M. Melloni, Ann. Chim. et Phys., lxv. p. 5.

MAGNETISM.

A PARTICULAR species of iron ore has long been remarkable for its property of attracting small pieces of iron, and causing them to adhere to its surface; it is called loadstone, or magnetic iron ore.

If a piece of this loadstone be carefully examined, it will be found that the attractive force for particles of iron is greatest at certain particular points of its surface, while elsewhere it is much diminished, or even altogether absent. These attractive points, or centres of greatest force, are denominated poles, and the loadstone itself is said to be endued with magnetic polarity.

If one of the poles of a natural loadstone be rubbed in a particular manner over a bar of steel, its characteristic properties will be communicated to the bar, which will then be found to attract iron filings like the loadstone itself. Further, the attractive force will be greatest at two points situated very near the extremities of the bar, and least of all towards the middle. The bar of steel so treated is said to be magnetized, or to constitute an artificial magnet.

When a magnetized bar or natural magnet is suspended at its centre in any convenient manner, so as to be free to move in a horizontal plane, it is always found to assume a particular direction with regard to the earth; one end pointing nearly north and the other nearly south. If the bar be moved from this position, it will tend to re-assume it, and after a few oscillations, settle at rest as before. The pole which points towards the astronomical north is usually distinguished as the north pole of the bar, and that which points southward, as the south pole. A suspended magnet, either natural or artificial, of symmetrical form, serves to exhibit certain phenomena of attraction and repulsion in the presence of a second magnet, which deserve particular attention. When a north pole is presented to a south pole, or a south pole to a north, attraction ensues between them; the ends of the bars approach each other, and, if permitted, adhere with considerable force; when on the other hand, a north pole is brought near a second north pole, or a south pole near another south pole, mutual repulsion is observed, and the ends of the bars recede from each other as far as possible. *Poles of an opposite name attract, and of a similar name repel each other.* Thus, a small bar or needle of steel, properly magnetized and suspended, and having its poles marked, becomes an instrument fitted not only to discover the existence of magnetic power in other bodies, but to estimate the kind of polarity affected by their different parts.

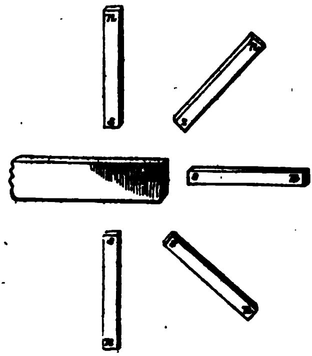
A piece of iron brought into the neighborhood of a magnet, acquires itself magnetic properties; the intensity of the power thus conferred depends upon that of the magnet and upon the interval which divides the two, becoming greater as that interval decreases, and greatest of all when in actual contact. The iron under these circumstances is said to be magnetized by induction, or influence, and the effect, which in an instant reaches its maximum, is at once destroyed by removing the magnet.

When steel is substituted for iron in this experiment, the inductive action is hardly at first perceptible, and only becomes manifest after the lapse of a certain time; in this state the steel bar may be removed from the magnet without loss of polarity. It becomes indeed a permanent magnet similar to the first, and retains its peculiar properties for an indefinite period.

A particular name is given to this resistance which steel always offers in

a greater or less degree both to the development of magnetism and its subsequent destruction; it is called *specific coercive power*.

Fig. 57.



The rule which regulates the induction of magnetic polarity in all cases is exceedingly simple, and most important to be remembered. The pole produced is always of the opposite name to that which produces it, a north pole developing south polarity, and a south pole, north polarity. The north pole of the magnet figured in the sketch induces south polarity in all the nearer extremities of the pieces of iron or steel which surround it, and a state similar to its own in all the more remote extremities. The iron thus magnetized is capable of exerting a similar inductive action on a second piece, and that upon a third, and so to a great number, the intensity of the force diminishing as the distance from the permanent magnet increases. It is in this way that a magnet is enabled to hold up a number of small pieces of iron, or a bunch of filings, each separate piece becoming a magnet for the time by induction.

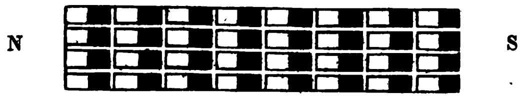
The only substances known which unequivocally exhibit magnetic effects are iron and certain of its compounds, and nickel, a closely allied metal.

Magnetic attractions and repulsions are not in the slightest degree interfered with by the interposition of substances destitute of magnetic properties. Thick plates of glass, shellac, metals, wood, or of any substances except those above-mentioned, may be placed between a magnet and a suspended needle, or a piece of iron under its influence, the distance being preserved without the least perceptible alteration in its attractive power or force of induction.

One kind of polarity cannot be exhibited without the other. If a magnetized bar of steel be broken at its neutral point, or in the middle, each of the broken ends acquires an opposite pole, so that both portions of the bar become perfect magnets; and if the division be still further carried, if the bar be broken into a hundred pieces, each fragment will be a complete magnet having its own north and south poles.

This experiment serves to show very clearly that the apparent polarity of the bar is the consequence of the polarity of each individual particle, the poles of the bar being merely points through which the resultants of all these forces pass; the large magnet is made up of an immense number of little magnets

Fig. 58.



regularly arranged side by side, all having their north poles looking one way, and their south poles the other. The middle portion of such a system cannot possibly exhibit attractive or repulsive effects on an external body, because each pole is in close juxtaposition with one of an opposite name and of equal power; hence their forces will be exerted in opposite directions and com-

pletely neutralize each other's influence. Such will not be the case at the extremities of the bar; there uncompensated polarity will be found capable of exerting its specific power.

This idea of regular polarization of particles of matter in virtue of a pair of opposite and equal forces, is not confined to magnetic phenomena; it is the leading principle in electrical science, and is constantly reproduced in some form or other in every discussion involving the consideration of molecular forces.

Artificial steel magnets are made in a great variety of forms; such as small, light needles, mounted with an agate cap for suspension upon a fine point; straight bars of various kinds; bars curved into the shape of a horse-shoe, &c. All these have regular polarity communicated to them by certain processes of rubbing or touching with another magnet, which require care, but are not otherwise difficult of execution. When great power is wished for, a number of bars may be screwed together, with their similar ends in contact, and in this way it is easy to construct permanent steel magnets capable of sustaining great weights. To prevent the gradual destruction of magnetic force, which would otherwise occur, it is usual to arm each pole with a piece of soft iron, or keeper, which, becoming magnetized by induction, serves to sustain the polarity of the bar, and even increase in some cases its energy.

The direction spontaneously assumed by a suspended needle indicates that the earth itself has the properties of an enormous magnet, whose south pole is in the northern hemisphere. The magnetic meridian of any place is a vertical plane with which the direction of a freely suspended needle coincides.

The magnetic meridian is not usually coincident with its geographical meridian, but makes with the latter a certain angle called the *variation* or *declination* of the needle; in other words, the magnetic poles are not situated within the line of the axis of rotation.

The amount of this declination of the needle from the true north and south not only varies at different places, but at the same place at different periods. Thus, at the commencement of the 17th century, the declination was eastward; in 1660, it was 0; that is, the needle pointed due north and south. Afterwards, it became westerly, slowly increasing until the year 1818, when it reached 24° 30′, since which time it has been slowly diminishing.

If a steel bar be supported on a horizontal axis passing exactly through its centre of gravity, it will of course remain equally balanced in any position in which it may happen to be placed; if the bar so adjusted be then magnetized, it will be found to take a permanent direction, the north pole being downwards, and the bar making an angle of about 70° with a horizontal plane passing through the axis. This is called the dip, or inclination of the needle, and shows the direction in which the force of terrestrial magnetism is most energetically exerted. The amount of this dip is variable in different latitudes; near the equator it is very small, the needle remaining nearly or quite horizontal; as the latitude increases, the dip becomes more decided, and over the magnetic pole, the bar becomes completely vertical. Such a situation is in fact to be found in the northern hemisphere, considerably to the westward of the geographical pole, in Prince Regent's Inlet, lat. 70° 5′ N. and longitude 96° 46′ W.; the dipping-needle has here been seen to point directly downwards, while the horizontal or compass-needle ceased to traverse. The position of the south magnetic pole has lately been determined by the observations of Captain Ross to be about lat. 73° S. and long. 130° E.

By observing a great number of points near the equator in which the dip becomes reduced to nothing, a line may be traced around the earth called the magnetic equator, and nearly parallel to this, on both sides, a number of smaller circles called lines of equal dip. These lines present great irregu-

larities when compared with the equator itself and the parallels of latitude, the magnetic equator deviating from the terrestrial one as much as 12° at its point of greatest divergence. Like the horizontal declination, the dip is also subject to change at the same place. Observations have not yet been made during sufficient time to determine accurately the law and rate of alteration, and great practical difficulties exist also in the construction of the instruments. In the year 1773 it was about 72°; at the present time it is near 69° 5 in London.

The inductive power of the magnetism of the earth may be shown by holding in a vertical position a bar of very soft iron; the lower end will be found to possess strong north polarity, and the upper, the contrary state. On reversing the bar, the poles are also reversed. All masses of iron whatever, when examined by a suspended needle, will be found in a state of magnetic polarity by the influence of the earth; iron columns, tools in a smith's shop, fire-irons, and other like objects, are all usually magnetic, and those made of steel, permanently so. On board ship the presence of so many large masses of iron, guns, anchors, water-tanks, &c., thus polarized by the earth, causes a derangement of the compass-needle to a very dangerous extent; happily, a plan has been devised for determining the amount of this local attraction in different positions of the ship and making suitable corrections.

The mariner's compass, which is nothing more than a suspended needle attached to a circular card marked with the points, was not in general use in Europe before the year 1300, although the Chinese have had it from very early antiquity. Its value to the navigator is now very much increased by correct observations of the exact amount of the declination in various parts of the world.

ELECTRICITY.

If glass, or amber, or sealing-wax, be rubbed with a dry cloth, it acquires the power of attracting light bodies, as feathers, dust, or bits of paper; this is the result of a new and peculiar condition of the body rubbed, called electrical excitation.

If a light downy feather be suspended by a thread of white silk, and a dry glass tube, excited by rubbing, be presented to it, the feather will be strongly attracted to the tube, adhere to its surface for a few seconds, and then fall off. If the tube be now excited anew and presented to the feather, the latter will be strongly repelled.

The same experiment may be repeated with shellac or resin; the feather in its ordinary state will be drawn towards the excited body, and after touching, again driven from it with a certain degree of force.

Now, let the feather be brought into contact with the excited glass, so as to be repelled by that substance, and let a piece of excited sealing-wax be presented to it; a degree of attraction will be observed far exceeding that exhibited when the feather is in its ordinary state. Or, again, let the feather be made repulsive for sealing-wax, and then the excited glass be presented; strong attraction will ensue.

The reader will at once see the perfect parallelism between the effects described and the phenomena of magnetism; the electrical excitement having a twofold nature like the opposite polarities of the magnet. A body to which one kind of excitement has been communicated is attracted by another body in the opposite state, and repelled by one in the same state. The excited glass and resin being to each other as the north and south poles of a pair of magnetized bars.

To distinguish these two different forms of excitement, terms are employed, which, although originating in some measure in theoretical views of the nature of the electrical disturbance, may be understood by the student as purely arbitrary and distinctive; it is customary to call the electricity manifested by glass *positive* or *vitreous*, and that developed in the case of shellac and bodies of the same class, *negative* or *resinous*. The kind of electricity depends in some measure upon the nature of the surface; smooth glass rubbed with silk or woolen becomes positive, but when ground or roughened by sand or emery, it acquires under the same circumstances a negative charge.

The repulsion shown by bodies in the same electrical state is taken advan-

Fig. 59.

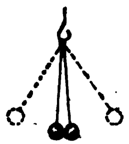
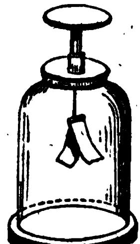


Fig. 60.

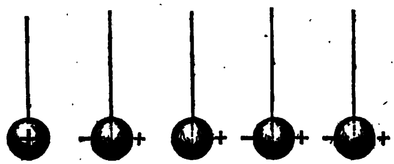


tage of to construct instruments for indicating electrical excitement and pointing out its kind. Two balls of alder-pith, hung by threads or very fine metal wires, serve this purpose in many cases; they open out when excited in virtue of their mutual repulsion, and show by the degree of divergence the extent to which the excitement has been carried. A pair of gold leaves suspended beneath a bell jar, and communicating with a metal cap above, constitute a much more delicate arrangement, and one of great value in all electrical investigations. These instruments are called electroscopes or electrometers; when excited by the communication of a known kind of electricity, they show, by an increased or diminished divergence, the state of an electrified body brought into their neighborhood.

One kind of electricity can no more be developed without the other than one kind of magnetism; the rubber and the body rubbed always assume opposite states, and the positive condition on the surface of a mass of matter is invariably accompanied by a negative state in all surrounding bodies.

The induction of magnetism in soft iron has its exact analogy in electricity; a body already electrified disturbs or polarizes the particles of all surrounding substances in the same manner, and according to the same law, inducing a state opposite to its own in the nearer portions, and a similar state in the more remote parts. A series of globes suspended by silk threads in the manner represented, will each become electric by induction when a charged body is brought near the end of the series, like so many pieces of iron in the vicinity of a magnet. The positive and negative signs are intended to represent the states.

Fig. 61.



The intensity of the electrical disturbance diminishes with the distance from the charged body; if this be removed or discharged, all the effects cease at once.

So far, the greatest resemblance may be traced between these two sets of phenomena; but here it seems to cease. Magnetic properties are enjoyed by two metals only, and a very few of their compounds, out of the whole list of substances known; electrical excitation is common to every form of matter, solid, liquid, and gaseous. The magnetic polarity of a piece of steel can awaken polarity in a second piece by the act of induction, and in so doing loses nothing whatever of its power; this is an effect completely different from the apparent transfer, or discharge of electricity constantly witnessed, which in the air and in liquids often gives rise to the appearance of a bright spark of fire. Bodies in which this discharge from particle to particle takes place very easily are called conductors; those, on the other hand, in which mere polarization takes place, and which resemble in this respect magnetized iron, are called insulators. The difference, however, is only one of degree, not of kind; the very best conductors offer a certain resistance to the electrical discharge, and the most perfect insulators permit it to a small extent. The metals are by far the best conductors; glass, silk, shellac, and dry gas, or

vapor of any sort, the very worst; and between these there are bodies of all degrees of conducting power.

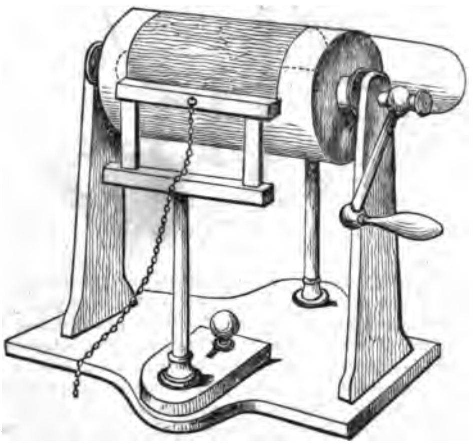
The time of transit of electrical wave through a chain of good conducting bodies of great length is so minute as to be altogether inappreciable. Miles of wire are traversed in an instant with a velocity of movement resembling that of light, and far too great to be made the subject of measurement by the means yet possessed by science.

Electrical excitation is *apparent* only upon the surfaces of bodies, or those portions directed towards other objects capable of assuming the opposite state. An insulated ball charged with positive electricity and placed in the centre of the room, is maintained in that state by the inductive action of the walls of the apartment, which immediately become negatively electrified; in the interior of the ball there is absolutely no electricity to be found, although it may be constructed of open metal gauze, with meshes half an inch wide. Even on the surface, the distribution of electrical force will not always be the same; it will depend upon the figure of the body itself, and its position with regard to surrounding objects. The polarity will always be highest in the projecting extremities of the same conducting mass, and greatest of all when these are attenuated to points, in which case the inequality becomes so great that discharge takes place to the air, and the excited condition cannot be maintained.

The construction and use of the common electrical machine, and other pieces of apparatus of great practical utility, will, by the aid of these principles, become intelligible.

A glass cylinder is mounted with its axis in a horizontal position, and pro-

Fig. 62.

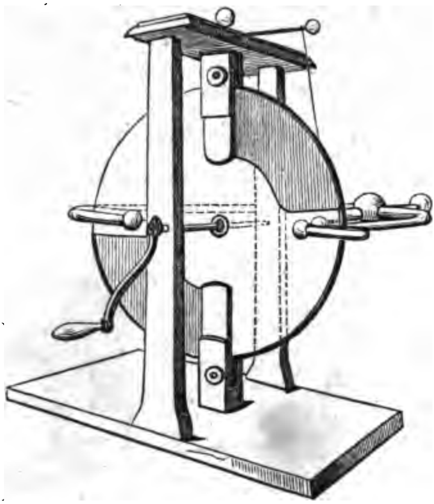


vided with a handle or winch by which it may be turned. A leather cushion is made to press by a spring against one side of the cylinder, while a large metal conducting body, armed with a number of points next the glass, occupies the other; both cushion and conductor are insulated by glass supports, and to the upper edge of the former a piece of silk is attached long enough to reach half round the cylinder. Upon the cushion is spread a quantity of a

soft amalgam of tin, zinc, and mercury,* mixed up with a little grease; this substance is found by experience to excite glass most powerfully. The cylinder as it turns thus becomes charged by friction against the rubber, and as quickly discharged by the row of points attached to the great conductor; and as the latter is also completely insulated, its surface speedily acquires a charge of positive electricity, which may be communicated by contact to other insulated bodies. The maximum effect is produced when the rubber is connected by a chain or wire with the earth. If negative electricity be wanted, the rubber must be insulated and the conductor discharged.

Another form of the electrical machine consists of a circular plate of glass moving upon an axis, and provided with two pairs of cushions or rubbers, attached to the upper and lower parts of the wooden frame, covered with amalgam, between which the plate moves with considerable friction. An insulated conductor, armed as before with points, discharges the plate as it turns, the rubbers being at the same time connected with the ground by the woodwork of the machine, or by a strip of metal. This modification of the apparatus is preferred in all cases where considerable power is wanted.

Fig. 63.



In the practical management of electrical apparatus, great care must be taken to prevent deposition of moisture from the air upon the surface of the glass supports; the slightest film of water is sufficient to destroy the power of insulation. The rubbers also must be carefully dried before use, and the amalgam renewed if needful; in damp weather much trouble is often experienced in bringing the machine into powerful action.

When a piece of iron is applied to a steel magnet, the polarity of the latter is exalted by the reaction of the newly developed force; in the same manner the intensity of the electrical charge on the surface of a conductor can be raised by the juxta-position of a second conducting body, the two being sepa-

* 1 part tin, 2 zinc, and 6 mercury.

rated by an insulating medium. If a disc of metal be connected with the machine, and a second disc placed opposite, within a few inches, and connected with the earth, the positive state of the first will be greatly augmented by the induced negative condition of the second; the limit is in this case, however, soon reached, because the intervening air easily permits spark-discharge to take place through its substance. With a solid insulating body, as glass or lac, this happens with much greater difficulty, the particles bearing a far higher degree of polarity without the same consequence. It is on this principle that instruments for the *accumulation* of electricity depend, among which the Leyden jar is the most important.

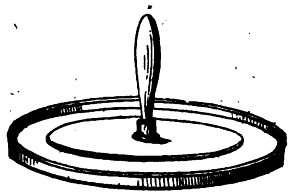
A thin glass jar is coated on both sides with tin-foil, care being taken to leave several inches of the upper part uncovered; a wire, terminating in a metallic knob, communicates with the internal coating; when the outside of the jar is connected with the earth, and the knob put in contact with the conductor of the machine, the inner and outer surfaces of the glass become respectively positive and negative, until a very great degree of intensity has been attained. On completing the connection between the two coatings by a metallic wire or rod, discharge occurs in the form of an exceedingly bright spark, accompanied by a loud snap; and if the body be interposed in the circuit, the peculiar and disagreeable sensation of the electric shock is felt at the moment of its completion.

Fig. 64.

By enlarging the dimensions of the jar, or by connecting together a number in such a manner that all may be charged and discharged simultaneously, the power of the apparatus may be greatly augmented. Thin wires of metal may be fused and dissipated; pieces of wood may be shattered, many combustible substances set on fire, and all the well-known effects of lightning exhibited upon a small scale.

The electric spark is often very conveniently employed in chemical inquiries for firing gaseous mixtures in close vessels. A small Leyden jar charged by the machine, is the most effective contrivance for this purpose, but, not unfrequently, a method may be resorted to which involves less preparation. This is by the use of the electrophorus. A round tray or dish of tinned plate is prepared, having a stout wire round its upper edge; the width may be about twelve inches, and the depth half an inch. This tray is filled with melted shellac, and the surface rendered as even as possible. A brass disc, with rounded edge, of about nine inches diameter, is also provided and fitted with an insulating handle. When a spark is wanted, the resinous plate is excited by striking with a dry, warm piece of flannel or a silk handkerchief; the cover is placed upon it, and touched by the finger. When the cover is raised, it is found so strongly charged by induction with positive electricity, as to give a bright spark; and as the resin is not discharged by the cover, which merely touches it at a few points, sparks may be drawn as often as may be wished.

Fig. 65.



It is not known to what cause the disturbance of the electrical equilibrium of the atmosphere is due; experiment has shown that the higher regions of the air are usually in a positive state, the intensity of which reaches a maximum at a particular period of the day. In cloudy and stormy weather the

distribution of the atmospheric electricity becomes much deranged, clouds near the surface of the earth often appearing in a negative state.

The circumstances of a thunder storm, exactly resemble those of the charge and discharge of a coated plate or jar; the cloud and the earth represent the two coatings, and the intervening air the bad conducting body or *dielectric*. The polarities of the opposed surfaces and of the insulating medium between them become raised by mutual induction, until violent disruptive discharge takes place through the air itself, or through any other bodies which may happen to be in the interval. When these are capable of conducting freely, the discharge is silent and harmless; but in other cases it often proves highly destructive. These dangerous effects are now in a great measure obviated by the use of lightning-rods attached to buildings, the erection of which, however, demands a number of precautions not always understood or attended to. The masts of ships may be guarded in like manner by metal conductors; Mr. Snow Harris has devised a most ingenious plan for the purpose, which is now adopted in the Royal Navy.

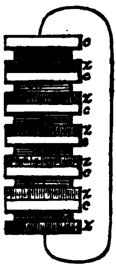
When two solid conducting bodies are plunged into a liquid which act upon them unequally, the electric equilibrium is also disturbed, the one acquiring the positive condition, and the other the negative. Thus, pieces of zinc and platinum put into dilute sulphuric acid, constitute an arrangement capable of generating electrical force; the zinc, being the metal attacked, becomes negative; and the platinum, remaining unaltered, assumes the positive condition; and on making a metallic communication in any way between the two plates, discharge ensues, as when the two surfaces of a coated and charged jar are put into connection.

No sooner, however, has this occurred, than the disturbance is repeated; and as these successive charges and discharges take place through the fluid and metals with inconceivable rapidity, the result is an apparently continuous action, to which the term *electrical current* is given.

It is necessary to guard against the idea which the term naturally suggests, of an actual bodily transfer of something through the substance of the conductors like water through a pipe; the real nature of all these phenomena is entirely unknown, and may perhaps remain so; the expression is convenient notwithstanding, and consecrated by long use; and with this caution, the very dangerous error of applying figurative language to describe an effect, and then seeking the nature of the effect from the common meaning of words, may be avoided.

The intensity of the electrical excitement developed by a single pair of metals and a liquid, is too feeble to affect the most delicate gold leaf electroscope; but by arranging a number of such alternations in a connected series, in such a manner that the direction of the current shall be the same in each, the intensity may be very greatly exalted. The two instruments invented by Volta, called the pile and crown of cups, depend upon this principle.

Fig. 66.

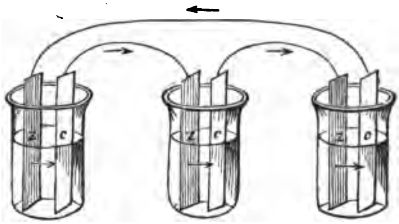


Upon a plate of zinc is laid a piece of cloth, rather smaller than itself, steeped in dilute acid, or any liquid capable of exerting chemical action upon zinc; upon this is placed a plate of copper, silver, or platinum; then a second piece of zinc, another cloth, and plate of inactive metal, until a pile of about twenty alternations has been built up. If the two terminal plates be now touched with wet hands, the sensation of the electric shock will be experienced; but unlike the momentary effect produced by the discharge of a jar, the sensation will be prolonged and

continuous, and with a pile of one hundred such pairs, excited by dilute acid, it will be nearly insupportable. When such a pile is insulated, the two extremities exhibit strong positive and negative states, and when connection is made between them by wires armed with points of hard charcoal or plumbago, the discharge takes place in the form of a bright enduring spark or stream of fire.

The second form of apparatus, or crown of cups, is precisely the same in principle although different in appearance. A number of cups or glasses are

Fig. 67.

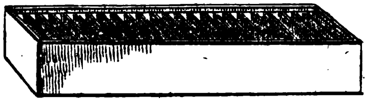


arranged in a row or circle, each containing a piece of active and a piece of inactive metal and a portion of exciting liquid; zinc, copper, and dilute sulphuric acid, for example. The copper of the first cup is connected with the zinc of the second, the copper of the second with the zinc of the third, and so to the end of the series. On establishing a communication between the first and last plates by means of a wire, or otherwise, discharge takes place as before.

When any such electrical arrangement consists merely of a single pair of conductors and an interposed liquid, it is called a simple circuit; when two or more alternations are concerned, the term compound circuit is applied; they are called also, indifferently, voltaic batteries. In every form of such apparatus, however complex it may appear, the direction of the current may be easily understood and remembered. The polarity or disturbance may be considered to commence at the surface of the metal attacked, and to be propagated through the liquid to the inactive conductor, and thence back again by the connecting wire, these extremities of the battery being always respectively negative and positive when the apparatus is insulated. In common parlance it is said, that the current in every battery in an active state starts from the metal attacked, passes through the liquid to the second metal or conducting body, and returns by the wire or other channel of communication: hence in the pile and crown of cups just described, the current *in* the battery is always from the zinc to the copper; and *out* of the battery, from the copper to the zinc, as shown by the arrows.

In the modification of Volta's original pile, made by Mr. Cruikshank, the zinc and copper plates are soldered together and cemented water-tight into a

Fig. 68.



mahogany trough, which thus becomes divided into a series of cells or compartments capable of receiving the exciting liquid. This apparatus is well fitted to exhibit effects of *tension*; to act upon the electroscope and give shocks; hence its advantageous employment in the application of electricity to medicine, as a very few minutes suffice to prepare it for use. The crown of cups was also put into a much more manageable form by Dr. Babington, and still further improved, as will hereafter be seen, by Dr. Wollaston. Subsequently, various alterations have been made by different experimenters with a view of obviating certain defects in the common batteries, of which a description will be found towards the middle of the volume.

The term galvanism, sometimes applied to this branch of electrical science, is used in honor of Professor Galvani, of Bologna, who, in 1790, made the very curious observation that convulsions could be produced in the limbs of a dead frog when certain metals were made to touch the nerve and muscle at the same moment. It was Volta, however, who pointed out the electrical origin of these motions, and although the explanation he offered of the source of the electrical disturbance is no longer generally adopted, his name is very properly associated with the invaluable instrument his genius gave to science.

In the year 1822 Professor Seebeck, of Berlin, discovered another source of electricity, to which allusion has already been made, namely inequality of temperature and conducting power in different metals placed in contact, or in the same metal in different states of compression and density. Even with a great number of alternations, the current produced is exceedingly feeble compared with that generated by the voltaic pile.

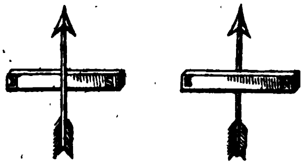
Two or three animals of the class of fishes, as the *torpedo*, or *electric ray*, and the *electrical eel* of South America, are furnished with a special organ or apparatus for developing electrical force, which is employed in defence, or in the pursuit of prey. Electricity is here seen to be closely connected with nervous power; the shock is given at the will of the animal, and great exhaustion follows repeated exertion of the power.

Although the fact that electricity is capable, under certain circumstances, both of inducing and of destroying magnetism, has long been known, from the effects of lightning on the compass-needle and upon small steel articles, as knives and forks, to which polarity has suddenly been given by the stroke, it was not until 1819 that the laws of these phenomena were discovered by Professor Œrsted, of Copenhagen, and shortly afterwards fully developed by M. Ampère.

The action which a current of electricity, from whatever source proceeding, exerts upon a magnetized needle, is quite peculiar. The poles or centres of magnetic force are neither attracted nor repelled by the wire carrying the current, but made to move *around* the latter, by a force which may be termed *tangential*, and which is exerted in a direction perpendicular at once to that of the current, and to the line joining the pole and the wire. Both poles of the magnet being thus acted upon at the same time, and in contrary directions, the needle is forced to arrange itself across the current, so that its axis, on the line joining the poles, may be perpendicular to the wire; and this is always the position which the needle will assume when the influence of terrestrial magnetism is in any way removed. This curious angular motion may even be shown by suspending a magnet in such a way that one only of its poles shall be subjected to the current; a permanent movement of rotation will continue as long as the current is kept up, its direction being changed by altering the pole, or reversing the current. The movable connections are made by mercury, into which the points of the conducting-wires dip. It is often of great practical consequence to be able to predict the direction in

which a particular pole shall move by a given current, because in all galvanoscopes, and other instruments involving these principles, the movement of the needle is taken as an indication of the direction of the circulating current, and this is easily done by a simple mechanical aid to the memory:—Let the current be supposed to pass through a watch from the face to the back: the motion of the north pole will be in the direction of the hands. Or a little piece of apparatus may be used if reference is often required; this is a piece of pasteboard, or other suitable material cut into the form of an arrow for indicating the current, crossed by a magnet having its poles marked, and

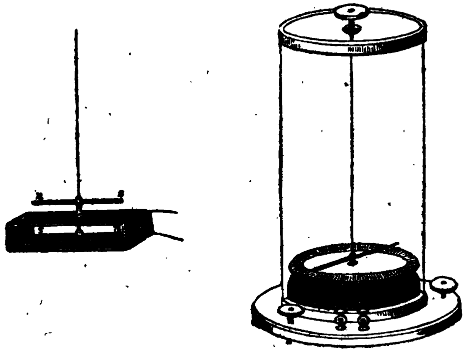
Fig. 69.



arranged in the true position with respect to the current. The direction of the latter in the wire of the galvanoscope can at once be known by placing the representative magnet in the direction assumed by the needle itself.

The common galvanoscope, consisting of a coil of wire having a compass-needle suspended on a point within it, is greatly improved by the addition of a second needle, as already in part described, and by a better mode of suspension, a long fibre of silk being used for the purpose. The two needles are of equal size, and magnetized as nearly as possible to the same extent; they are then immovably fixed together, parallel, and with their poles opposed, and hung with the lower needle in the coil and the upper one above it. The advantage gained is twofold; the system is *astatic*, unaffected, or nearly so, by the magnetism of the earth; and the needles being both acted upon in the same manner by the current, are urged with much greater force than one alone would be, all the actions of every part of the coil being strictly concurrent. A divided circle is placed below the upper needle, by which the angu-

Fig. 70.

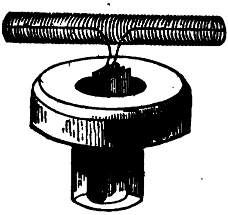


lar motion can be measured, and the whole is enclosed in glass to shield the needle from the agitation of the air.

The action between the pole and the wire is mutual, as may be shown by rendering the wire itself movable and placing a magnet in its vicinity; on completing the circuit the wire will be put in motion, and, if the arrangement permits, rotate around the magnetic pole.

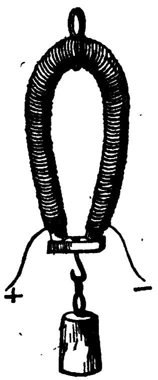
A little consideration will show, that from the peculiar nature of the electro-dynamic force, a wire carrying a current, bent into a spiral or helix, must possess all the properties of an ordinary magnetized bar, its extremities being attracted and repelled by the poles of a magnet. Such is really found to be the case, as may be proved by a variety of arrangements, among which it will be sufficient to cite the beautiful little apparatus of Professor De la Rive. A short, wide glass tube is fixed into a cork ring of considerable size; a little voltaic battery, consisting of a single pair of copper and zinc plates, is fitted to the tube, and to these the ends of the spiral are soldered. On filling the tube with dilute acid and floating the whole in a large basin of water, the helix will be observed to arrange itself in the magnetic meridian, and on trial it will be found to obey a magnet held near it, in the most perfect manner, as long as the current circulates.

Fig. 71.



When an electric current is passed at right angles to a piece of iron or steel, the latter acquires magnetic polarity, either temporary or permanent as the case may be, the direction of the current determining the position of the poles. This effect is prodigiously increased by causing the current to circulate a number of times round the bar, which then acquires extraordinary magnetic power. A piece of soft iron, worked into the form of a horse-shoe, and surrounded by a coil of copper wire covered with silk or cotton for the purpose of insulation, furnishes an excellent illustration of the inductive energy of the current in this respect; when the ends of the wire are put into communication with a small voltaic battery of a single pair of plates, the iron instantly becomes so highly magnetic as to be capable of sustaining a very heavy weight.

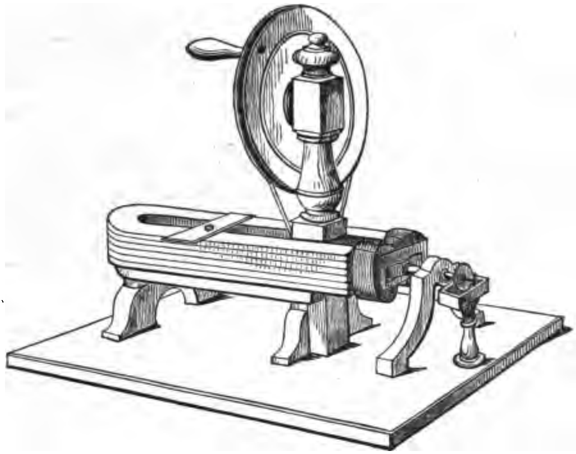
Fig. 72.



A current of electricity can thus develop magnetism in a transverse direction to its own; in the same manner, magnetism can call into activity electric currents. If the two extremities of the coil of the electro-magnet above described, be connected with a galvanoscope, and the iron magnetized by the application of a permanent steel horse-shoe magnet to the ends of the bar, a momentary current will be developed in the wire, and pointed out by the movement of the needle. It lasts but a single instant, the needle returning after a few oscillations to a state of rest. On removing the magnet, whereby the polarity of the iron is at once destroyed, a second current or wave will become apparent, but in the opposite direction to that of the first. By employing a very powerful steel magnet, surrounding its iron keeper or armature with a very long coil of wire, and then making the armature itself rotate in front of the faces of the magnet, so that its induced polarity shall be rapidly

reversed, magneto-electric currents may be produced, of such intensity as to give bright sparks and most powerful shocks, and exhibit all the phenomena of voltaic electricity. Fig. 73 represents a very powerful arrangement of this kind.

Fig. 73.



When two covered wires are twisted together or laid side by side for some distance, and a current transmitted through the one, a momentary electrical wave will be induced in the other in the reverse direction, and on breaking connexion with the battery, a second single wave will become evident by the aid of the galvanoscope, in the same direction as that of the primary current. These curious induced currents, sometimes acquire a degree of intensity superior to that of the battery-current itself. The effect described may even occur in a single wire.

M. Ampère discovered in the course of his investigations a number of extremely interesting phenomena resulting from the action of electrical currents on each other, which become evident when arrangements are made for giving mobility to the conducting-wires. He found, that when two currents flowing in the same direction were made to approach each other, strong attraction took place between them, and when in opposite directions, an equally strong repulsion. These effects, which are not difficult to demonstrate, have absolutely no relation that can be traced to ordinary electrical attractions and repulsions, from which they must be carefully distinguished; they are purely *dynamic*, having to do with electricity in motion. M. Ampère founded upon this discovery a most beautiful and ingenious hypothesis of magnetic actions in general, which explains very clearly the influence of the current upon the needle.

The polarity of the earth is now generally supposed to be due to electrical currents circulating within and around it, and which may perhaps be called into existence by the unequal heating of the surface by the rays of the sun.

The electricity exhibited under certain peculiar circumstances by a jet of

steam, first observed by mere accident, but since closely investigated by Mr. Armstrong, and also by Mr. Faraday, is now referred to the friction, not of the pure steam itself, but of particles of condensed water, against the interior of the exit tube. It is very doubtful whether *mere evaporation* can cause electrical disturbance, and the hope first entertained that these phenomena would throw light upon the cause of electrical excitement in the atmosphere, is now abandoned. The steam is usually positive, if the jet-pipe be constructed of wood or clean metal, but the introduction of the smallest trace of oily matter causes a change of sign. The intensity of the charge is, *cæteris paribus*, increased with the elastic force of the steam; already effects have been obtained very far surpassing those of the most powerful plate electrical machines ever constructed.*

* The student will find in the *Experimental Researches* of Mr. Faraday, some time since published in a collected form, an inexhaustible fund of information on many of these curious subjects. The complete revolution which the discoveries there described have effected in the received views of electrical phenomena greatly increases the difficulty at the present moment of explaining in a clear and satisfactory manner the elementary parts of the science of statical electricity.

The articles Magnetism and Electro-magnetism, by Dr. Roget, in the tracts of the Society for the Diffusion of Useful Knowledge, may be also consulted with advantage.

PART II.

CHEMISTRY OF ELEMENTARY BODIES.

The term *element* or *elementary substance* is applied in chemistry to those forms or modifications of matter which have hitherto resisted all attempts to decompose them. Nothing is ever meant to be affirmed concerning their real nature; they are simply elements to us at the present time; hereafter, by new methods of research, or by new combinations of those already possessed by science, many of the substances which now figure as elements may possibly be shown to be compounds; this has already happened, and may again take place.

The elementary bodies, at present recognized, amount to fifty-five in number; of these, about forty belong to the class of metals. The distinction between metals and non-metallic substances, although very convenient for purposes of description, is entirely arbitrary, since the two classes graduate into each other in the most complete manner.

It will be proper to commence with the latter and least numerous division. The elements are named as in the subjoined table, which, however, does not indicate the order in which they will be discussed.

Non-metallic Elements.	Elements of intermediate characters.	Metals.	
Oxygen	Phosphorus	Antimony	Yttrium
Hydrogen	Arsenic	Chromium	Bismuth
Nitrogen	Tellurium	Vanadium	Tin
Chlorine		Tungsten	Mercury
Iodine		Molybdenum	Silver
Bromine		Columbium	Lead
Fluorine		Titanium	Barium
Carbon		Uranium	Strontium
Silicon		Cerium	Calcium
Boron		Lantanum *	Magnesium
Sulphur		Platinum	Zinc
Selenium		Palladium	Cadmium
		Rhodium	Nickel
		Iridium	Cobalt
		Osmium	Copper
		Gold	Iron
		Aluminum	Manganese
		Glucinum	Lithium
		Zirconium	Sodium
		Thorium	Potassium

* To which may be added the eight lately discovered metals, viz: Didymium, Erbium, Terbium, Norium, Pelopium, Niobium, Ilmenium, and Ruthenium.—R. B.

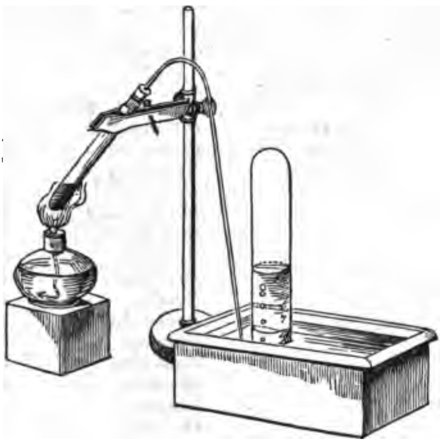
OXYGEN.

Whatever plan of classification, founded on the natural relations of the elements, be adopted, in the practical study of chemistry, it will always be found most advantageous to commence with the consideration of the great constituents of the ocean and the atmosphere.

Oxygen was discovered in the year 1774, by Scheele, in Sweden, and Dr. Priestley, in England, independently of each other, and described under the terms *empyreal air* and *vital air*. * The name oxygen† was given to it by Lavoisier some time afterwards. Oxygen exists in a free and uncombined state in the atmosphere, mingled with another gaseous body, nitrogen; no direct means exist, however, for separating it from the latter, and accordingly, it is always obtained for purposes of experiment by decomposing certain of its compounds, which are very numerous.

The red oxide of mercury, or *red precipitate* of the old writers, may be employed with this view. In this substance the attraction which holds together the mercury and the oxygen is so feeble that simple exposure to heat suffices to bring about decomposition. The red precipitate is placed in a short tube of hard glass, to which is fitted a perforated cork, furnished with a piece of narrow glass tube, bent as in the figure. The heat of a spirit-lamp being applied to the substance, decomposition speedily commences, globules of metallic mercury collect in the cool part of the wide tube, which answers the purpose of a retort, while gas issues in considerable quantity from the apparatus. This gas is collected and examined by the aid of the pneumatic trough, which consists of a vessel of water provided with a shelf, upon which stand the jars or bottles destined to receive the gas, filled with water and

Fig. 74.



inverted. By keeping the level of the liquid above the mouth of the jar, the water is retained in the latter by the pressure of the atmosphere, and entrance

* Noticed though not isolated by Cardan, (1557,) Boyle, (1670,) Mayow, (1674,) but first obtained pure and described by Priestley, (1774,) under the name of *dephlogisticated air*, and by Scheele, (1775,) under that of *empyreal air*.—R. B.

† From ὀξύς, acid, and γεννάω, I give rise to.

of air prevented. When brought over the extremity of the gas-delivering tube, the bubbles of gas arising through the water collect in the upper part of the jar and displace the liquid. As soon as one jar is filled, it may be removed, still keeping its mouth below the water-level, and another substituted. The arrangement is shown in fig. 74.

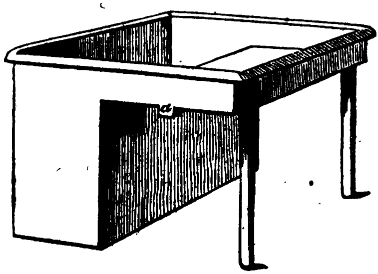
The experiment described is more instructive as an excellent case of the resolution by simple means of a compound body into its constituents, than valuable as a source of oxygen gas. A better and more economical method is to expose to heat in a retort, or flask furnished with a bent tube, a portion of the salt called chlorate of potash. A common Florence flask serves perfectly well, the heat of a spirit-lamp being sufficient. The salt melts and decomposes with ebullition, yielding a very large quantity of pure oxygen gas, which may be collected in the way above described. The white saline residue in the flask is chloride of potassium. This plan, which is very easy of execution, is always adopted when very pure gas is required for analytical purposes.

A third method, very good when perfect purity is not demanded, is to heat to redness, in an iron retort or gun-barrel, the black oxide of manganese of commerce, which under these circumstances suffers decomposition, although not to the extent manifest in the red precipitate.

If a little of the black oxide of manganese be finely powdered and mixed with chlorate of potash,* and this mixture heated in a flask or retort by a lamp, oxygen will be disengaged with the utmost facility, and at a far lower temperature than when the chlorate alone is used. All the oxygen comes from the chlorate, the manganese remaining quite unaltered. The materials should be well dried in a capsule before their introduction into the flask. This experiment affords an instance of an effect by no means rare, in which a body seems to act by its mere presence, without taking any obvious part in the change brought about.

Whatever method be chosen—and the same remark applies to the collection of all other gases by similar means—the first portions of gas must be suffered to escape, or be received apart, as they are contaminated by the atmospheric air of the apparatus. The practical management of gases is a point of great importance to the chemical student, and one with which he must endeavor to familiarize himself. The water-trough just described is one of the

Fig. 75.

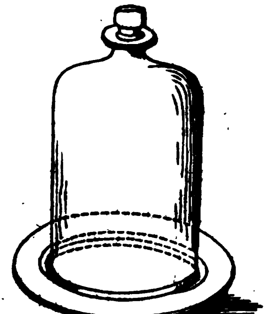


most indispensable articles of the laboratory, and by its aid all experiments on gases are carried on when the gases themselves are not sensibly acted upon

* In the proportion of one or two parts of the former to ten of the latter.—R. B.

by water. The trough is best constructed of japanned copper, the form and dimensions being regulated by the magnitude of the jars. It should have a firm shelf, so arranged as to be always about an inch below the level of the water, and in the shelf a groove should be made, about half an inch in width, and the same in depth, to admit the extremity of the delivery tube beneath the jar, which stands securely upon the shelf. When the pneumatic trough is required of tolerably large dimensions, it may with great advantage have the form and disposition represented in the cut (fig. 75); one end of the groove spoken of, which crosses the shelf or shallow portion, is shown at *a*.

Fig. 76.

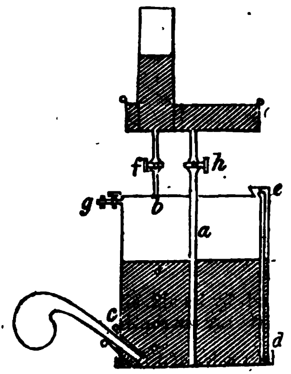


Gases are transvased from jar to jar with the utmost facility, by first filling the vessel into which the gas is to be passed with water, inverting it, carefully retaining its mouth below the water-level, and then bringing beneath it the aperture of the jar containing the gas. On gently inclining the latter, the gas passes by a kind of inverted decantation into the second vessel. When the latter is narrow, a funnel may be placed loosely in its neck, by which loss of gas will be found to be prevented.

A jar wholly or partially filled with gas at the pneumatic trough may be removed by placing beneath it a shallow basin, or even a common plate, so as to carry away enough water to cover the edge of the jar; and gas, especially oxygen, may be so preserved for many hours without material injury.

Gas-jars are often capped at the top and fitted with a stop-cock for transferring to bladders or caoutchouc bags. When such a vessel is to be filled with water, it may be slowly sunk in an upright position in the well of the pneumatic trough, the stop-cock being open to allow the air to escape, until the water reaches the brass cap. The cock is then to be turned, and the jar lifted upon the shelf and filled with gas in the usual way. If the trough be not deep enough for this manœuvre, the mouth may be applied to the stopcock and the vessel filled by sucking out the air until the water rises to the cap. In all cases it is proper to avoid as much as possible wetting the stop-cocks and other brass apparatus.

Fig. 77.



Mr. Pepys contrived some years ago an admirable piece of apparatus for storing and retaining large quantities of gas. It consists of a drum or reservoir of sheet copper, surmounted by a shallow trough or cistern, the communication between the two being made by a couple of tubes, *a b*, furnished with cocks, *f h*, one of which, *a*, passes nearly to the bottom of the drum, as shown in the sectional sketch. A short wide open tube, *c*, is inserted obliquely near the bottom of the vessel, into which a plug may be tightly screwed. A stop-cock, *g*, near the top serves to transfer gas to a bladder or tube apparatus. A glass

water-gauge, *e*, *d*, affixed to the side of the drum, and communicating with both top and bottom, indicates the level of the liquid within.

To use the gas-holder, the plug is first to be screwed into the lower opening, and the drum completely filled with water. All three stop-cocks are then to be closed, and the plug removed. The pressure of the atmosphere retains the water in the gas-holder; and if no air-leakage occur, the escape of water is inconsiderable. The extremity of the delivery-tube or retort is now to be well pushed through the open aperture into the drum, so that the bubbles of gas rise without hinderance to the upper part, displacing the water which flows out in the same proportion into a vessel placed for its reception. When the drum is filled, or enough gas has been collected, the tube is withdrawn, and the plug screwed into its place.

When a portion of the gas is to be transferred to a jar, the latter is to be filled with water at the pneumatic trough, carried by the help of a basin or plate to the cistern of the gas-holder, and placed over the shorter tube. On opening the cock of the neighboring tube, the hydrostatic pressure of the column of water will cause condensation in the gas, and increase its elastic force, so that on gently turning the cock beneath the jar, it will ascend into the latter in a rapid stream of bubbles. The jar, when filled, may again have the plate slipped beneath it, and be removed without difficulty.

Oxygen when free or uncombined, is only known in the gaseous state, all attempts to reduce it to the liquid or solid condition by cold and pressure having completely failed. It is, when pure, colorless, tasteless, and inodorous; it is the sustaining principle of animal life, and of all the ordinary phenomena of combustion.

Bodies which burn in the air burn with greatly increased splendor in oxygen gas. If a taper be blown out, and then introduced while the wick remains red hot, it is instantly rekindled: a slip of wood or a match is relighted in the same manner. This effect is highly characteristic of oxygen, there being but one other gas which possesses the same property; and this is easily distinguished by other means. The experiment with the match is also constantly used as a rude test of the goodness of the gas when it is about to be collected from the retort, or when it has stood some time in contact with water exposed to the air.

When a bit of barkey charcoal is affixed to a wire and plunged with a single point red-hot into a jar of oxygen, it burns with great brilliancy, throwing off beautiful scintillations until, if the oxygen be in excess, it is completely consumed. An iron wire, or, still better, a steel watch-spring, armed at its extremity with a bit of lighted amadou, and introduced into a vessel of good gas, exhibits a most beautiful appearance of combustion. If the experiment be made in a jar standing on a plate, the fused globules of black oxide of iron fix themselves in the glaze of the latter after falling through a stratum of water half an inch in depth. Kindled sulphur burns with great beauty in oxygen, and phosphorus, under similar circumstances, exhibits a splendor which the eye is unable to support.

In these and many other similar cases which might be mentioned, the same ultimate effect is produced as in atmospheric air; the action is, however more energetic from the absence of the gas which in the air dilutes the oxygen and enfeebles its chemical powers. The process of respiration in animals is an effect of the same nature as common combustion. The blood contains substances which burn by the aid of the oxygen thus introduced into the system. When this action ceases, life becomes extinct.

Oxygen is, bulk for bulk, a little heavier than atmospheric air, which is usually taken as the standard of unity among gases. Its specific gravity is

expressed by the number 1·1057;* 100 cubic inches at 60°, and under the mean pressure of the atmosphere, that is, 30 inches of mercury, weigh 34·29 grains.

It has been already remarked, that to determine with the least degree of accuracy the specific gravity of a gas is an operation of very great practical difficulty, but at the same time of very great importance. There are several methods which may be adopted for this purpose; the one below-mentioned appears, on the whole, to be the simplest and best. It requires, however, the most scrupulous care, and the observance of a number of minute precautions, which are absolutely indispensable to success.

The plan of the operation is simply this: A large glass globe is to be filled with the gas to be examined, in a perfectly pure and dry state, having a known temperature, and an elastic force equal to that of the atmosphere at the time of the experiment. The globe so filled is to be weighed. It is then to be exhausted at the air-pump as far as convenient, and again weighed. Lastly, it is to be filled with dry air, the temperature and pressure of which are known, and its weight once more determined. On the supposition that the temperature and elasticity are the same in both cases, the specific gravity is at once obtained by dividing the weight of the gas by that of the air.

The globe or flask must be made very thin, and fitted with a brass cap, surmounted by an excellent stop-cock. A delicate thermometer is placed in the inside of the globe. The gas must be generated at the moment, and conducted at once into the previously exhausted vessel, through a long tube filled with fragments of pumice moistened with oil of vitriol, or some other extremely hygroscopic substance, by which it is freed from all moisture. As the gas is necessarily generated under some pressure, the elasticity of that contained in the filled globe will slightly exceed the pressure of the atmosphere; and this is an advantage, since by opening the stop-cock for a single instant when the globe has attained a temperature of equilibrium, the tension becomes exactly that of the air, so that all barometrical correction is avoided, unless the pressure of the atmosphere should sensibly vary during the time occupied by the experiment. It is hardly necessary to remark, that the greatest care must also be taken to purify and dry the air used as the standard of comparison, and to bring both gas and air to as nearly as possible the same temperature, to obviate the necessity of a correction, or at least to diminish almost to nothing the errors involved by such process.

The compounds formed by the direct union of oxygen with other bodies, bear the general name of oxides; these are very numerous and important. They are conveniently divided into three principal groups or classes. The first division contains all those oxides which resemble in their chemical relations potash, soda, or the oxide of silver or of lead; these are denominated *alkaline* or *basic* oxides, or sometimes, *salifiable bases*. The oxides of the second group have properties exactly opposed to those of the bodies mentioned; oil of vitriol and phosphoric acid may be taken as the types or representatives of the class: they are called *acids*, and they tend strongly to unite with the basic oxides. When this happens, what is called a *salt* is generated, as sulphate of potash, or phosphate of oxide of silver, each of these substances being compounded of a pair of oxides, one of which is highly basic and the other highly acid.

Then, there remains a third group of what may be termed *neutral* bodies, from their little disposition to enter into combination. The black oxide of manganese, already mentioned, is an excellent example.

It very frequently happens that a body is capable of uniting with oxygen in several proportions, forming a series of oxides, to which it is necessary to

* Dumas, Ann. Chim. et Phys., 3d Series, iii. p. 275.

give distinguishing names. The rule in such cases is very simple, at least when the oxides of the metals are concerned. In such a series it is always found that one out of the number has a strongly-marked basic character; to this, the term *protoxide* is given. The compounds next succeeding receive the names of *deutoxide*, *tritoxide*, &c., from the Greek numerals, the different grades of oxidation being thus indicated. It is usual to call the highest oxide, not having distinctly acid characters, *peroxide*, from the Latin prefix, signifying excess. Any compound containing less oxygen than the protoxide, is called a *sub-oxide*.

Other terms are occasionally used; thus, when two oxides of the same substance occur, if the second contain, as is often the case, twice as much oxygen as the first, the expression *binoxide* is sometimes used to point out this relation. *Superoxide* or *hyperoxide* is a word sometimes applied to the higher neutral oxides which easily pass into protoxides by losing oxygen.

HYDROGEN.

Hydrogen is always obtained for experimental purposes by deoxidizing water, of which it forms the characteristic component.*

If a tube of iron or porcelain, containing a quantity of filings or turnings of iron, be fixed across a furnace, and its middle portion be made red hot, and then the vapor of water transmitted over the heated metal, a large quantity of permanent gas will be disengaged from the tube, and the iron will become converted into oxide, and acquire an increase in weight. The gas is hydrogen; it may be collected over water and examined.

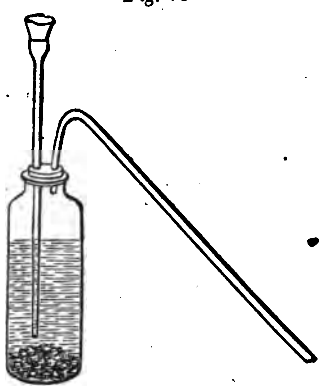
When zinc is put into water, chemical action of the liquid upon the metal is imperceptible, but if a little sulphuric acid be added, decomposition of the water ensues, the oxygen unites with the zinc, forming oxide of zinc, which is instantly dissolved by the acid, while the hydrogen, previously in union with that oxygen, is disengaged in the gaseous form. The reaction is represented in the subjoined diagram.

Water { Hydrogen ———————————— Free.
Water { Oxygen ——————
Zinc ———————————— oxide of zinc } Sulphate of
Sulphuric acid ———————————— } oxide of zinc.

It is not easy to explain the fact of the ready decomposition of water by zinc, in presence of an acid or other substance which can unite with the oxide so produced; it is, however, a kind of reaction of very common occurrence in chemistry.

The simplest method of preparing the gas is the following:—A wide-necked bottle is chosen, and fitted with a sound cork, perforated by two holes for the reception of a small tube funnel reaching nearly to the bottom of the bottle, and a piece of bent glass tube to convey away the disengaged gas. Granulated zinc, or scraps of the malleable metal are put into the bottle, together with a little water, and sulphuric acid slowly added by the funnel, the point of which should dip into

Fig. 78



* Hence the name, from ὕδωρ, water, and γεννάω.

the liquid. The evolution of gas is easily regulated by the supply of acid, and when enough has been discharged to expel the air of the vessel, it may be collected over water into a jar, or passed into a gas-holder. In the absence of zinc, filings of iron or small nails may be used, but with less advantage.

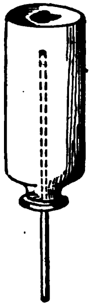
A little practice will soon enable the pupil to construct and arrange a variety of useful forms of apparatus, in which bottles and other articles always at hand are made to supersede more costly instruments. Glass tube, purchased by weight of the maker, may be cut by scratching with a file and then applying a little force with both hands. It may be softened and bent, when of small dimensions, by the flame of a spirit-lamp, or even a candle or gas-jet. Corks may be perforated by a heated wire, and the hole rendered smooth and cylindrical by a round file, or the ingenious cork-borer of Dr. Mohr, now to be had of most instrument-makers, may be used instead. Lastly, in the event of bad fitting, or unsoundness in the cork itself, a little yellow wax melted over the surface, or even a little grease applied with the finger, renders it sound and air-tight, when not exposed to heat.

Hydrogen is colorless, tasteless, and inodorous when quite pure; when prepared from commercial zinc it has a slight smell, which is due to impurity, and when iron has been used, the odor becomes very strong and disagreeable. It is inflammable, burning when kindled with a pale yellowish flame, and evolving much heat, but very little light. The result of the combustion is water. It is even less soluble in water than oxygen, and has never been liquefied. Although destitute of poisonous properties, it is incapable of sustaining life.

In point of specific gravity, hydrogen is the lightest substance known; Dumas and Boussingault place its density petween ·0691 and ·0695;* hence 100 cubic inches will weigh, under ordinary circumstances of pressure and temperature, 2.14 grains.

When a gas is much lighter or much heavier than atmospheric air, it may often be collected and examined without the aid of the pneumatic trough. A bottle or narrow jar may be filled with hydrogen without much admixture of air, by inverting it over the extremity of an upright tube delivering the gas. In a short time, if the supply be copious, the air will be wholly displaced and the vessel filled. It may now be removed, the vertical position being carefully retained, and closed by a stopper or glass plate. If the mouth of the jar be wide, it must be partially closed by a piece of card-board during the operation. This method of collecting gases by displacement is often extremely useful. Hydrogen was formerly used for filling air balloons, being made for the purpose on the spot from zinc or iron and dilute sulphuric acid. Its use is now superseded by that of coal-gas, which may be made very light by employing a high temperature in the manufacture. Although far inferior to pure hydrogen in buoyant power, it is found in practice to possess advantages over that substance, while its greater density is easily compensated by increasing the magnitude of the balloon.

Fig. 79.



There is a very remarkable property enjoyed by gases and vapors in general, which is seen in a high degree of intensity in the case of hydrogen; this is what is called *diffusive power*. If two bottles containing gases, which do not act chemically upon each other at common temperature, be connected by a narrow tube (fig. 80), and left for some time, they will be found, at the expiration of a certain period, depending much upon the narrowness of the tube and

* Ann. Chim. et Phys., 3d Series, viii. p. 201.

its length, uniformly mixed, even though the gases differ greatly in density, and the system has been arranged in a vertical position, with the heaviest gas downwards. Oxygen and hydrogen can thus be made to mix, in a few hours, against the action of gravity, through a tube a yard in length, and not more than one-quarter of an inch in diameter; and the fact is true of all other gases which are destitute of direct action upon each other.

Fig. 80.

If a vessel be divided into two portions by a diaphragm or partition of porous earthenware or dry plaster of Paris, and each half filled with a different gas, diffusion will immediately commence through the pores of the dividing substance, and will continue until perfect mixture has taken place. All gases, however, do not permeate the same porous body, or, in other words, do not pass through narrow orifices with the same degree of facility. Mr. Graham, to whom we are indebted for a very valuable investigation of this interesting subject, has established the existence of a very simple relation between the rapidity of diffusion and the density of the gas, which is expressed by saying that the diffusive power varies inversely as the square root of the density of the gas itself. Thus, in the experiment supposed, if one half of the vessel be filled with hydrogen, and the other with oxygen, the two gases will penetrate the diaphragm at a very different rate; four cubic inches of hydrogen will pass into the oxygen side, while one cubic inch of oxygen travels in the opposite direction. The densities of the two gases are to each other in the proportion of 1 to 16; their relative rates of diffusion will be inversely as the square roots of these numbers, or 4 to 1.

By making the diaphragm of some flexible material, as a piece of membrane, the accumulation of the lighter gas on the side of the heavier may be rendered evident by the bulging of the membrane. The simplest and most striking method of making the experiment is by the use of Mr. Graham's diffusion-tube. This is merely a piece of white glass tube ten or twelve inches in length, having one of its extremities closed by a plate of plaster of Paris about half an inch thick, and well dried. When the tube is filled by displacement with hydrogen, and then set upright in a glass of water, the level of the liquid rises in the tube so rapidly, that its movement is apparent to the eye, and speedily attains a height of several inches above the water in the glass. The gas is actually rarefied by its superior diffusive power over that of the external air.

Fig. 81.

It is impossible to over-estimate the importance in the great economy of Nature of this very curious law affecting the constitution of gaseous bodies; it is the principal mean by which the atmosphere is preserved in a uniform state, and the accumulation of poisonous gases and exhalations in towns and other confined localities prevented.

A distinction must be carefully drawn between real diffusion through small apertures, and the apparently similar passage of gases through wet or moist membranes and other substances, which is really due to temporary liquefaction or solution of the gas, and is an effect completely different from diffusion properly so called. For example, the diffusive power of carbonic acid into atmospheric air is very small, but it passes into the latter through a wet bladder with the utmost ease, in virtue of its solubility in the water with

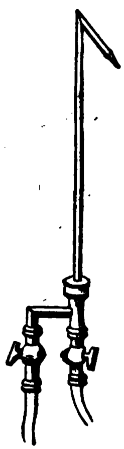
which the membrane is moistened. It is by such a process that the function of respiration is performed; the aëration of the blood in the lungs, and the disengagement of its carbonic acid, are effected through wet membranes; the blood is never brought into actual contact with the air, but receives its supply of oxygen, and disembarrasses itself of carbonic acid by this kind of spurious diffusion.

The high diffusive power of hydrogen against air renders it impossible to retain that gas for any length of time in a bladder or caoutchouc bag; it is even unsafe to keep it long in a gas-holder, lest it should become mixed with air by slight accidental leakage, and rendered explosive.

It has been stated, that although the light emitted by the flame of pure hydrogen is exceedingly feeble, yet the temperature of the flame is very high. This temperature may be still further exalted by previously mixing the hydrogen with as much oxygen as it requires for combination, that is, as will presently be seen, exactly half its volume. Such a mixture burns like gunpowder, independently of the external air. When raised to the requisite temperature for combination, the two gases unite with explosive violence. If a strong bottle, holding not more than half a pint, be filled with such a mixture, the introduction of a lighted match or red-hot wire determines in a moment the union of the gases. By certain precautions, a mixture of oxygen and hydrogen can be burned at a jet without communication of fire to the contents of the vessel; the flame is in this case *solid*.

A little consideration will show, that all ordinary flames burning in the air or in pure oxygen are, of necessity, hollow. The act of combustion is nothing more than the energetic union of the substance burned with the surrounding oxygen; and this union can only take place at the surface of the burning body. Such is not the case, however, with the flame now under consideration; the combustible and the oxygen are already mixed, and only require to have their temperature a little raised to cause them to combine in every part. The flame so produced is very different in physical characters from that of a simple jet of hydrogen or any other combustible gas; it is long and pointed, and very remarkable in appearance.

Fig. 82.



The safety-jet of Mr. Hemming, the construction of which involves a principle not yet discussed, may be adapted to a common bladder containing the mixture, and held under the arm, and the gas forced through the jet by a little pressure. Although the jet, properly constructed, is believed to be safe, it is best to use nothing stronger than a bladder, for fear of injury in the event of an explosion. The gases are often contained in separate reservoirs, a pair of large gas-holders, for example, and only suffered to mix in the jet itself, as in the contrivance of Professor Daniell; in this way all danger is avoided. The eye speedily becomes accustomed to the peculiar appearance of the true hydro-oxygen flame, so as to permit the supply of each gas to be exactly regulated by suitable stop-cocks attached to the jet, (fig. 82.)

A piece of thick platinum wire introduced into the flame of the hydro-oxygen blow-pipe melts with the greatest ease; a watch-spring, or small steel file burns with the utmost brilliancy, throwing off showers of beautiful sparks; an incombustible oxidized body, as magnesia or lime, becomes so intensely ignited, as to glow with a light insupportable to the eye, and to be susceptible of employment as a most powerful illuminator, as a substitute for

the sun's rays in the solar microscope, and for night signals in trigonometrical surveys.

Fig. 83.

If a long glass tube, open at both ends, be held over a jet of hydrogen, a series of musical sounds are sometimes produced by the partial extinction and rekindling of the flame by the ascending current of air. These little explosions succeed each other at regular intervals, and so rapidly as to give rise to a musical note, the pitch depending chiefly upon the length and diameter of the tube.

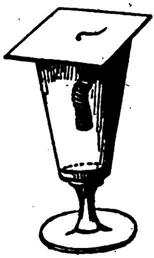
Although oxygen and hydrogen may be kept mixed at common temperatures for any length of time without combination taking place, yet, under particular circumstances, they unite quietly and without explosion. Some years ago Professor Döbereiner of Jena, made the curious observation that finely-divided platinum possessed the power of determining the union of the gases, and more recently Mr. Faraday has shown that the state of minute division is by no means indispensable, since rolled plates of the metal had the same property, provided their surfaces were absolutely clean. Neither is the effect strictly confined to platinum; other metals, as palladium and gold, and even stones and glass, enjoy the same property, although to a far inferior degree, since they often require to be aided by a little heat. When a piece of platinum foil which has been cleaned by hot oil of vitriol and thorough washing with distilled water, is thrust into a jar containing a mixture of oxygen and hydrogen standing over water, combination of the two gases immediately begins, and the level of the water rapidly rises, and the platinum becomes so hot, that drops of water accidentally falling upon it enter into ebullition. If the metal be very thin and exceedingly clean, and the gases very pure, then its temperature rises, after a time, to actual redness, and the residue of the mixture explodes. But this is an effect altogether accidental, and dependent upon the high temperature of the platinum, which high temperature has been produced by the preceding quiet combination of the two bodies. When the platinum is reduced to a state of division, and its surface thereby much extended, it becomes immediately red-hot in a mixture of hydrogen and oxygen, or of hydrogen and air; a jet of hydrogen thrown upon a little of the spongy metal contained in a glass or capsule becomes at once kindled, and on this principle, machines for the production of instantaneous light have been constructed. These, however, only act well when constantly used; the spongy platinum is apt to become damp by absorption of moisture from the air, and its power is then for the time lost.

The best explanation that can be given of these curious effects, is to suppose that solid bodies in general have, to a greater or less extent, the property of condensing gases upon their surfaces, and that this faculty is enjoyed pre-eminently by certain of the non-oxidizable metals, as platinum and gold. Oxygen and hydrogen may thus under these circumstances be brought, as it were, within the sphere of their mutual attractions by a temporary increase of density, whereupon combination ensues.

Coal-gas and ether or alcohol vapor may be made to exhibit the phenomenon of quiet oxidation under the influence of this remarkable surface action. A close spiral of slender platinum wire, or a roll of thin foil heated to dull redness and then held in a jet of coal-gas, becomes strongly ignited, and remains in that state as long as the supply of mixed gas and air is kept up, the temperature being maintained by the heat disengaged in the act of union. Sometimes the metal becomes white hot, and then the gas takes fire.

A very pleasing experiment may be made by attaching such a coil of wire to a card, and suspending it in a glass containing a few drops of ether, having

Fig. 84.



previously made it red-hot in the flame of a spirit lamp. The wire continues to glow until the oxygen of the air is exhausted, giving rise to the production of an irritating vapor which attacks the eyes. The combustion of the ether is in this case but partial; a portion of its hydrogen is alone removed, and the whole of the carbon left untouched.

A coil of thin platinum wire may be placed over the wick of a spirit lamp, or a ball of spongy platinum sustained just above the cotton; on lighting the lamp and then blowing it out as soon as the metal appears red-hot, slow combustion of the spirit drawn up by the capillarity of the wick will take place, accompanied by the pungent vapors just mentioned, which may be modified, and even rendered agreeable, by dissolving in the liquid some sweet-smelling essential oil or resin.

Hydrogen forms numerous compounds with other bodies, although it is greatly surpassed in this respect not only by oxygen, but by many of the other elements. The chemical relations of hydrogen tend to place it beside the metals. The great discrepancy in physical properties is perhaps more apparent than real. Hydrogen is yet unknown in the solid condition, while on the other hand, the vapor of the metal mercury is as transparent and colorless as hydrogen itself. This vapor is only about seven times heavier than atmospheric air, so that the difference in this respect is not nearly so great as that in the other direction between air and hydrogen.

There are two oxides of hydrogen, namely, *water*, and a very peculiar substance, discovered in the year 1818, by M. Thénard, called *peroxide of hydrogen.*

It appears, that the composition of water was first demonstrated in the year 1781 by Mr. Cavendish, but the discovery of the exact proportions in which oxygen and hydrogen unite in generating that most important compound has from time to time to the present day occupied the attention of some of the most distinguished cultivators of chemical science. There are two distinct methods of research in chemistry, the *analytical*, or that in which the compound is resolved into its elements, and the *synthetical*, in which the elements are made to unite and produce the compound. The first method is of much more general application than the second, but in this particular instance both may be employed, although the results of the synthesis are most valuable.

Fig. 85.

The most elegant example of an analysis of water would probably be found in its decomposition by voltaic electricity. When water is acidulated so as to render it a conductor, and a portion interposed between a pair of platinum plates connected with the extremities of a voltaic apparatus of moderate power, decomposition of the liquid takes place in a very interesting manner; oxygen, in a state of perfect purity, is evolved from the water in contact with the plate belonging to the copper end of the battery, and hydrogen, equally pure, is disengaged at the plate connected with the zinc extremity, the middle portions of liquid remaining apparently unaltered. By placing small graduated jars over the platinum plates, the gases can be collected, and their quantities determined. The figure in the margin will show at a glance the whole ar-

rangement; the conducting wires pass through the bottom of the glass cup, and away to the battery.

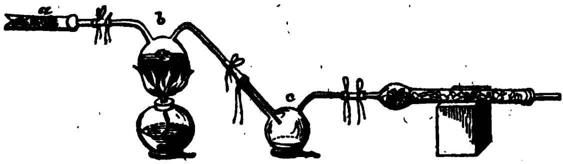
When this experiment has been continued a sufficient time, it will be found that the volume of the hydrogen is a *very* little above twice that of the oxygen; were it not for the accidental circumstance of oxygen being sensibly more soluble in water than hydrogen, the proportion of two to one by measure would come out exactly.

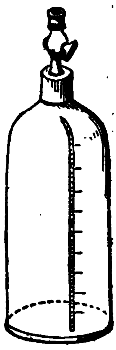
Fig. 86.

When oxygen and hydrogen, both as pure as possible, are mixed in the proportions mentioned, passed into a strong glass tube filled with mercury, and exploded by the electric spark, all the mixture disappears, and the mercury is forced up into the tube, filling it completely. The same experiment may be made with the explosion-vessel or eudiometer of Mr. Cavendish. The instrument is exhausted at the air-pump, and then filled from a capped jar with the mixed gases; on passing an electric spark by the wires shown at *a*, explosion ensues, and the glass becomes bedewed with moisture, and if the stop-cock be then opened under water, the latter will rush in and fill the vessel, leaving merely a bubble of air, the result of imperfect exhaustion.

The process upon which most reliance is placed is that in which pure oxide of copper is reduced at a red heat by hydrogen, and the water so formed collected and weighed. This oxide suffers no change by heat alone, but the momentary contact of hydrogen, or any common combustible matter at a high temperature, suffices to reduce a corresponding portion to the metallic state. Fig. 87 will serve to convey some idea of the arrangement adopted in researches of this kind.

Fig. 87.





A copious supply of hydrogen is procured by the action of dilute sulphuric acid upon the purest zinc that can be obtained; the gas is made to pass in succession through solutions of silver and strong caustic potash, by which its purification is completed. After this, it is conducted through a tube three or four feet in length, filled with fragments of pumice-stone steeped in concentrated oil of vitriol, or with anhydrous phosphoric acid. These substances have such an extraordinary attraction for aqueous vapor that they dry the gas completely during its transit. The extremity of this tube is shown at *a*. The dry hydrogen thus arrives at the part of the apparatus containing the oxide of copper, represented at *b*; this consists of a two-necked flask of very hard white glass, maintained at a red heat by a spirit-lamp placed beneath. As the decomposition proceeds, the water produced by the reduction of the oxide begins to condense in the second neck of the flask, whence it drops into the receiver *c*, provided for the purpose. A second desiccating tube prevents the loss of aqueous vapor by the current of gas which passes in excess.

Before the experiment can be commenced, the oxide of copper, the purity of which is well ascertained, must be heated to redness for some time in a current of dry air; it is then suffered to cool, and very carefully weighed with the flask. The empty receiver and second drying tube are also weighed, the disengagement of gas set up, and when the air has been displaced, heat slowly applied to the oxide. The action is at first very energetic; the oxide often exhibits the appearance of ignition; as the decomposition proceeds, it becomes more sluggish, and requires the application of a good deal of heat to effect its completion.

When the process is at an end, and the apparatus perfectly cool, the stream of gas is discontinued; dry air is drawn through the whole arrangement, and lastly, the parts are disconnected and re-weighed. The loss of the oxide of copper gives the oxygen; the gain of the receiver and its drying-tube indicates the water, and the difference between the two, the hydrogen.

A set of experiments, made in Paris in the year 1820,* by MM. Dulong and Berzelius, gave as a mean result for the composition of water by weight, 8·009 parts oxygen to 1 part hydrogen; numbers so nearly in the proportion of 8 to 1, that the latter have usually been assumed to be true.

Quite recently the subject has been re-investigated by M. Dumas† with the most scrupulous precision, and the above supposition fully confirmed. The composition of water may therefore be considered as established; it contains by weight 8 parts oxygen to 1 part hydrogen, and by measure, 1 volume oxygen to 2 volumes hydrogen. The densities of the gases, as already mentioned, correspond very closely with these results.

The physical properties of water are too well known to need lengthened description; it is, when pure, colorless, and transparent, destitute of taste and odor, and an exceedingly bad conductor of electricity of low tension. It attains its greatest density towards 40° F., freezes at 32°, and boils under the pressure of the atmosphere at 212°. It evaporates at all temperatures, one cubic inch at 62° F. weighs 252·45 grains. It is 815 times heavier than air; an imperial gallon weighs 70,000 grains, or 10 lbs. avoirdupois. To all ordinary observation, water is incompressible; very accurate experiments have nevertheless shown, that it does yield to a small extent when the power employed is very great; the diminution of volume for each atmosphere of pressure being about 51 millionths of the whole.

Steam, or vapor of water in its state of greatest density at 212°, compared with air at the same temperature, and possessing an equal elastic force, has a specific gravity expressed by the fraction ·625. In this condition it may be represented as containing in every two volumes, two volumes of hydrogen and one volume of oxygen.

Water seldom or never occurs in nature in a state of perfect purity; even the rain which falls in the open country contains a trace of ammoniacal salt, while rivers and springs are invariably contaminated to a greater or less extent with soluble matters, saline and organic. Simple filtration through a porous stone or a bed of sand will separate suspended impurities, but distillation alone will free the liquid from those that are dissolved. In the preparation of distilled water, which is an article of large consumption in the scientific laboratory, it is proper to reject the first portions which pass over, and to avoid carrying the distillation to dryness; the process may be conducted in a metal still furnished with a worm or condenser of silver or tin; lead must not be used.

The ocean is the great recipient of the saline matter carried down by the rivers which drain the land; hence the vast accumulation of salts. The fol-

* Ann. Chim. et Phys., xv. p. 386.

† Ann. Chim. et Phys., 3d Series, viii. p. 189.

lowing table will serve to convey an idea of the ordinary composition of sea-water; the analysis is by Dr. Schweitzer* of Brighton, the water being that of the Channel:—

1000 grains contained

Water	964·745
Chloride of sodium	27·059
Chloride of potassium	·766
Chloride of magnesium	3·666
Bromide of magnesium	·029
Sulphate of magnesia	2·296
Sulphate of lime	1·406
Carbonate of lime	·033
Traces of iodine and ammoniacal salt	
	1000·

Its specific gravity was found to be 1·0274 at 60°.

Sea-water is liable to variations of density and composition by the influence of local causes, such as the proximity of large rivers or masses of melting ice, and other circumstances.

Natural springs are often impregnated to a great extent with soluble substances derived from the rocks they traverse; such are the various mineral waters scattered over the whole earth, and to which medicinal virtues are attributed. Some of these hold protoxide of iron in solution, and are effervescent from carbonic acid gas; others are alkaline, probably from traversing rocks of volcanic origin; some contain a very notable quantity of iodine or bromine. Their temperatures also are as variable as their chemical nature. A tabular notice of some of the most remarkable of these waters will be found in the Appendix.

Water enters into direct combination with other bodies, forming a class of compounds called *hydrates;* the action is often very energetic, much heat being evolved, as in the case of the slaking of lime, which is really the production of a hydrate of that base. Sometimes the attraction between the water and the second body is so great that the compound is not decomposable by any heat that can be applied; the hydrates of potash and soda, and of phosphoric acid furnish examples. Oil of vitriol is a hydrate of sulphuric acid, from which the water cannot be thus separated.

Water very frequently combines with saline substances in a less intimate manner than that above described, constituting what is called water of crystallization, from its connection with the geometrical figure of the salt. In this case it is easily driven off by the application of heat.

Lastly, the solvent properties of water far exceed those of any other liquid known. Among salts, a very large proportion are soluble to a greater or less extent, the solubility usually increasing with the temperature, so that a hot saturated solution deposits crystals on cooling. There are a few exceptions to this law, one of the most remarkable of which is common salt, the solubility of which is nearly the same at all temperatures.

Water dissolves gases, but in very unequal quantities; some, as hydrogen, oxygen, and atmospheric air, are but little acted upon; others, as ammonia and hydrochloric acid, are absorbed to an enormous extent; and between these extremes there are various intermediate degrees. Generally, the colder the water, the more gas does it dissolve; a boiling heat disengages the whole, if the gas be not very soluble.

When water is heated in a strong vessel to a temperature above that of the

* Phil. Mag., July, 1839.

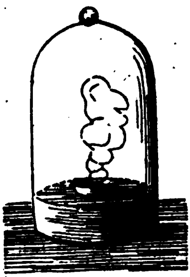
ordinary boiling point, its solvent powers are still further increased. Dr. Turner enclosed in the upper part of a high-pressure steam-boiler worked at 300° F., pieces of plate and crown glass. At the expiration of four months the glass was found completely corroded by the action of the water; what remained was a white mass of silica, destitute of alkali, while stalactites of siliceous matter, above an inch in length, depended from the little wire cage which enclosed the glass. This experiment tends to illustrate the changes which may be produced by the action of water at a high temperature in the interior of the earth upon felspathic and other rocks. Something of the sort is manifest in the Geyser springs of Iceland, which deposit siliceous sinter.*

Peroxide of hydrogen, sometimes called *oxygenated water*, is an exceedingly interesting substance, but unfortunately very difficult of preparation. It is formed by dissolving the peroxide of barium in dilute hydrochloric acid, carefully cooled by ice, and then precipitating the barytes by sulphuric acid; the excess of oxygen of the peroxide, instead of being disengaged as gas, unites with a portion of the water and converts it into peroxide of hydrogen. The peroxide of barium itself is prepared by exposing pure baryta contained in a red-hot porcelain tube to a stream of oxygen. The solution of peroxide of hydrogen may be concentrated under the air-pump receiver until it acquires the specific gravity of 1·45. In this state it presents the aspect of a colorless, transparent, inodorous liquid, possessing remarkable bleaching powers. It is very prone to decomposition; the least elevation of temperature causes effervescence due to the escape of oxygen gas; near 212° it is decomposed with explosive violence. Peroxide of hydrogen contains exactly twice as much oxygen as water, or 16 parts to 1 part of hydrogen.

NITROGEN.

Nitrogen† constitutes about $\frac{4}{5}$ths of the atmosphere, and enters into a great variety of combinations. It may be prepared for the purpose of experiment by several methods. One of the simplest of these is to burn out the oxygen from a confined portion of air by phosphorus, or by a jet of hydrogen.

Fig. 88.



A small porcelain capsule is floated on the water of the pneumatic trough, and a piece of phosphorus placed in it and set on fire. A bell-jar is then inverted over the whole and suffered to rest on the shelf of the trough, so as to project a little over its edge. At first, the heat causes expansion of the air of the jar, and few bubbles are expelled, after which the level of the water rises considerably. When the phosphorus becomes extinguished by exhaustion of the oxygen, and time has been given for the subsidence of the cloud of finely-divided, snow-like phosphoric acid, which floats in the residual gas, the nitrogen may be decanted into other vessels and its properties examined.

Prepared by the foregoing process, nitrogen is contaminated by a little vapor of phosphorus which communicates its peculiar odor. A preferable method, is to fill a porcelain tube with turnings of copper, or, still better, with the spongy metal obtained by reducing the oxide by hydrogen; to heat this tube to redness, and then pass through it a stream of atmospheric air, the oxygen of which is entirely removed during its progress by the heated copper.

* Phil. Mag., Oct. 1834.

† *i. e.* Generator of nitre; also called azote, from ἀ, privative, and ζωη, life.

If chlorine gas be passed into solution of ammonia, the latter substance, which is a compound of nitrogen with hydrogen, is decomposed; the chlorine combines with the hydrogen, and the nitrogen is set free with effervescence. In this manner very pure nitrogen can be obtained. In making this experiment it is necessary to stop short of saturating or decomposing the whole of the ammonia, otherwise there will be great risk of accident from the formation of an exceedingly dangerous explosive compound formed by the contact of chlorine with an ammoniacal salt.

Nitrogen is destitute of color, taste, and smell; it is a little lighter than air, its density being, according to Dumas, ·972. 100 cubic inches, at 60°, and 30 inches barometer, will therefore weigh 30·14 grains. Nitrogen is incapable of sustaining combustion or animal existence, although, like hydrogen, it has no positive poisonous properties; neither is it soluble to any notable extent in water, or in caustic alkali; it is in fact best characterized by negative properties.

The exact composition of the atmosphere has repeatedly been made the subject of experimental research. Besides nitrogen and oxygen, the air contains a little carbonic acid, a very variable proportion of aqueous vapor, a trace of ammonia, and *perhaps* a little carburetted hydrogen. The oxygen and nitrogen are in a state of mixture, not of combination, yet their ratio is always uniform. Air has been brought from the summits of Mont Blanc and Chimborazo, and from the plains of Egypt; it has been brought from an elevation of 21,000 feet by the aid of a balloon; it has been collected and examined in London and Paris, and many other districts: still the proportions of oxygen and nitrogen remain unaltered; the diffusive energy of the gases being adequate to maintain this perfect uniformity of mixture. The carbonic acid, on the contrary, being much influenced by local causes, varies considerably. In the following table the proportions of oxygen and nitrogen are given on the authority of M. Dumas, and the carbonic acid on that of De Saussure; the ammonia, the discovery of which is due to Liebig, is too small in quantity for direct estimation.

Composition of the Atmosphere.

	By weight.	By measure.
Nitrogen	77 parts.	79·19
Oxygen	23	20·81
	100	100

Carbonic acid, from 3·7 measures to 6·2 measures, in 10,000 measures of the air.
Aqueous vapor variable, depending much upon the temperature.
Ammonia, a trace.
100 cubic inches of pure and dry air, weigh, according to Dr. Prout, 31·0117 grains; the temperature being 60° F. and the barometer standing at 30 inches.

The analysis of air is best effected by passing it over finely-divided copper contained in a tube of hard glass, carefully weighed, and then heated to redness; the nitrogen is suffered to flow into an exhausted glass globe, also previously weighed. The increase of weight after the experiment gives the information sought.

An easier, but less accurate method, consists in introducing into a graduated tube, standing over water, a known quantity of the air to be examined, and then passing into the latter a stick of phosphorus affixed to the end of a wire, (fig. 89.) The whole is left about 24 hours, during which the oxygen is slowly

Fig. 89.

but completely absorbed, after which the phosphorus is withdrawn and the residual gas read off.

Another plan is to mix the air with hydrogen and pass an electric spark; after explosion the volume of gas is read off and compared with that of the air employed. Since the analysis of gaseous bodies by explosion is an operation of great importance in practical chemistry, it may be worth while describing the process in detail, as it is applicable, with certain obvious variations, to a number of analogous cases.

The most convenient form of apparatus for the purpose is the siphon eudiometer of Dr. Ure; (fig. 90.) This consists of a stout glass tube, having an internal diameter of about one-third of an inch, closed at one end, and bent into the form represented in the drawing. Two pieces of platinum wire melted into the glass near the closed extremity, serve to give passage to the spark. The closed limb is carefully graduated. When required for use, the instrument is filled with mercury and inverted into a vessel of the same fluid. A quantity of the air to be examined is then introduced, the manipulation being precisely the same as with experiments over water; the open end is stopped with a finger, and the air transferred to the closed extremity.

Fig. 90.

The instrument is next held upright, and after the level of the mercury has been made equal on both sides by displacing a portion from the open limb by thrusting down a piece of stick, the volume of air is read off. This done, the open part of the tube is again filled up with mercury, closed with the finger, inverted into the liquid metal, and a quantity of pure hydrogen introduced, equal as nearly as can be guessed to about half the volume of the air. The eudiometer is once more brought into an erect position, the level of the mercury equalized, and the volume again read off; the quantity of hydrogen added is thus accurately ascertained. All is now ready for the explosion; the instrument is held in the way represented, the open end being firmly closed by the thumb, while the knuckle of the fore-finger touches the nearer platinum wire; the spark is then passed by the aid of a charged jar or a good electrophorus, and explosion ensues. The air confined by the thumb in the open part of the tube acts as a spring and moderates the explosive effect. Nothing now remains but to equalize the level of the mercury by pouring a little more into the instrument, and then, to read off the volume for the last time.

What is required to be known from this experiment is the *diminution* the mixture suffers by explosion; for since the hydrogen is in excess, and since that substance unites with oxygen in the proportion by measure of two to one, one-third part of that diminution must be due to the oxygen contained in the air introduced. As the amount of the latter is known, the proportion of oxygen it contains thus admits of determination. The case supposed will render this clear.

Air introduced	. . . .	100 measures.
Air and hydrogen	. . . . . .	150
Volume after explosion	. . . . .	87
Diminution	. . . .	63

$\frac{63}{3} = 21$; oxygen in the hundred measures.

The working pupil will do well to acquire dexterity in the use of this valuable instrument, by practising the transference of gas or liquid from the one limb to the other, &c. In the analysis of combustible gases by explosion with oxygen, solution of caustic potash is often required to be introduced into the closed part.

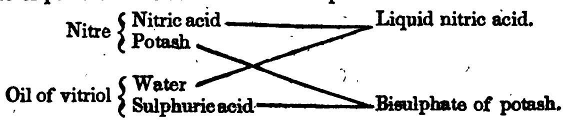
Compounds of Nitrogen and Oxygen.

There are not less than five distinct compounds of nitrogen and oxygen, thus named and constituted.

	Composition by Weight.	
	Nitrogen.	Oxygen.
Protoxide of nitrogen*	14·06	8
Deutoxide, or binoxide of nitrogen† .	14·06	16
Hyponitrous acid‡	14·06	24
Nitrous acid§	14·06	32
Nitric acid	14·06	40

Nitric or *Azotic acid.*—In certain parts of India, and also in other hot dry climates where rain is rare, the surface of the soil is occasionally covered by a saline efflorescence, like that sometimes apparent on newly-plastered walls; this substance collected, dissolved in hot water, the solution filtered and made to crystallize, furnishes the highly important salt known in commerce as nitre or saltpetre; it is a compound of nitric acid and potash. To obtain liquid nitric acid, equal weights of powdered nitre and oil of vitriol are introduced into a glass retort, and heat applied by means of an Argand gas-lamp or charcoal chauffer. A flask, cooled by a wet cloth, is adapted to the retort, to serve for a receiver. No luting of any kind must be used.

As the distillation advances, the red fumes which first arise disappear, but towards the end of the process again become manifest. When this happens, and very little liquid passes over, while the greater part of the saline matter of the retort is in a state of tranquil fusion, the operation may be stopped; and when the retort is quite cold, water may be introduced to dissolve out the bisulphate of potash. The reaction is thus explained.



Liquid nitric acid so obtained has a specific gravity of about 1·5; it has a golden yellow color, which is due to nitrous or hyponitrous acid held in solution, the pure acid being colorless. It is exceedingly corrosive, and stains the

* Otherwise called nitrous oxide.
† Otherwise called nitric oxide.
‡ Called by Mr. Graham nitrous acid.
§ Called by Mr. Graham peroxide of nitrogen.—The nomenclature adopted in the text is that employed in Dr. Turner's very valuable treatise.

skin yellow. It boils at about 187° Fahrenheit. Poured upon red-hot powdered charcoal, it causes brilliant combustion; and when added to a little warm oil of turpentine, acts upon that substance with such energy as to set it on fire. Many of the metals are attacked by nitric acid with great violence, if a little water be added, the very strong acid seeming to have little power in this respect. Organic substances, also, as starch or sugar, decompose nitric acid, and cause the evolution of abundance of red vapor.

Acid of the density of 1·5 to 1·52 is the strongest that can be obtained; it then consists of 54·06 parts real acid, and 9 parts water, being a definite compound.* The acid itself, in its absolute form, is unknown; it is an hypothetical substance. On adding different proportions of water to the strong liquid acid above described, one or two other definite combinations of acid and water appear to be generated, remarkable for the differences observed in their boiling and freezing points.

Nitric acid forms with bases a very extensive and important group of salts, the nitrates, which are remarkable for being all soluble in water. The hydrated acid is of great use in the laboratory, and also in many branches of industry.

The acid prepared in the way described is apt to contain traces of chlorine from common salt in the nitre, and sometimes of sulphate from accidental splashing of the pasty mass in the retort. To discover these impurities, a portion is diluted with four or five times its bulk of distilled water, and divided between two glasses. Solution of nitrate of silver is dropped into the one, and solution of nitrate of barytes into the other; if no change ensue in either case, the acid is free from the impurities mentioned.

Nitric acid has been formed in small quantity by a very curious process, namely, by passing a series of electric sparks through a portion of air; water, or an alkaline solution being present. The amount of acid so formed after many hours is very minute; still it is not impossible that powerful discharges of atmospheric electricity may sometimes occasion a trifling production of nitric acid in the air.

Nitric acid is not so easily detected in solution in small quantities as many other acids. Owing to the solubility of all its compounds, no *precipitant* can be found for this substance. One of the best tests is its power of bleaching a solution of indigo in sulphuric acid when boiled with that liquid. The absence of chlorine must be ensured in this experiment, by means which will hereafter be obvious, otherwise the result is equivocal.

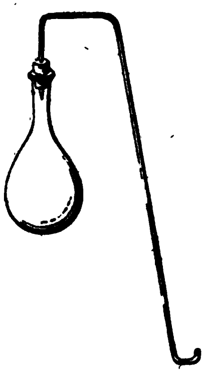
Protoxide of nitrogen; Nitrous oxide; (laughing gas.)—When solid nitrate of ammonia is heated in a retort or flask,† (fig. 91,) furnished with a perforated cork and bent tube, it is resolved into water and nitrous oxide. The nature of the decomposition will be understood from the subjoined diagram.

Nitrate of Ammonia 80·12	Nitric acid 54·06	Nitrogen	14·06	Protox. nitrogen 22·06
		Oxygen	8·	
		Oxygen	8·	
		Oxygen	24·	
	Ammonia 17·06	Nitrogen	14·06	Protox. nitrogen 22·06
		Hydrogen	3·	Water 27
	Water 9			Water 9

* According to Ure's table, and also to Mr. Phillip's, nitric acid of the specific gravity of 1·5 is composed of 54 anhydrous acid and 13·5 water; but according to Mitscherlich, when of 1·521 it contains 9 parts of water. Strong nitric attracts moisture from the air and diminishes in density. Its density is also altered by ebullition; a concentrated acid, by losing more acid than watery vapor, becomes less dense, until its specific gravity is 1·42, while a weak acid loses water until it acquires the density of 1·42, when it distils, unchanged, at the temperature of 248° F.—R. B.

† Florence oil-flasks, which may be purchased for a very trifling sum, constitute exceedingly useful vessels for chemical purposes, and often supersede retorts, or other expensive apparatus. They are rendered still more valuable by cutting the neck

Fig. 91.



No particular precaution is required in the operation, save due regulation of the heat, and the avoidance of tumultuous disengagement of the gas.

Protoxide of nitrogen is a colorless, transparent, and almost inodorous gas, of distinctly sweet taste. Its specific gravity is 1·525; 100 cubic inches weigh 47·29 grains. It supports the combustion of a taper or a piece of phosphorus with almost as much energy as pure oxygen; it is easily distinguished, however, from that gas by its solubility in cold water, which dissolves nearly its own volume; hence it is necessary to use tepid water in the pneumatic trough or gas-holder, otherwise great loss of gas will ensue. Nitrous oxide has been liquefied, but with difficulty; it requires, at 45° Fahrenheit, a pressure of 50 atmospheres.* When mixed with an equal volume of hydrogen, and fired by the electric spark in the eudiometer, it explodes with violence, and liberates its own measure of nitrogen. Every two volumes of the gas must consequently contain two volumes of nitrogen, and one volume of oxygen, the whole being condensed or contracted one-third; a constitution resembling that of vapor of water.

The most remarkable feature in this gas is its intoxicating power upon the animal system. It may be respired, if quite pure, or merely mixed with atmospheric air, for a short time without danger or inconvenience. The effect is very transient, and is not followed by depression.

Deutoxide or *binoxide of nitrogen.*—Clippings or turnings of copper are put into the apparatus employed for preparing hydrogen,† together with a little water, and nitric acid added by the funnel until brisk effervescence is excited. The gas may be collected over cold water, as it is not sensibly soluble.

The reaction is a simple de-oxidation of some of the nitric acid by the copper; the metal is oxidized, and the oxide so formed is dissolved by another portion of the acid. Nitric acid is very prone to act thus upon certain metals.

The gas obtained in this manner is colorless and transparent; in contact with air or oxygen gas it produces deep red fumes which are readily absorbed by water; this character is sufficient to distinguish it from all other gaseous bodies. A lighted taper plunged into the gas is extinguished; lighted phosphorus, however, burns in it with great brilliancy.‡

The specific gravity of deutoxide of nitrogen is 1·039; 100 cubic inches weigh 32·22 grains. It contains equal measures of oxygen and nitrogen gases united without condensation. When this gas is passed into a solution of protoxide of iron it is absorbed in large quantity, and a deep brown or nearly black liquid produced, which seems to be a definite compound of the two substances. The compound is again decomposed by boiling.

Hyponitrous acid.—Four measures of deutoxide of nitrogen are mixed with one measure of oxygen, and the gases, perfectly dry, exposed to a temperature of 0° Fah. They condense to a thin mobile liquid, which at that degree of

smoothly round with a hot iron, softening it in the flame of a good Argand gas-lamp, and then turning over the edge so as to form a lip, or border. The neck will then bear a tight fitting cork without risk of splitting.

* Protoxide of nitrogen has been solidified by M. I. Natterrer of Vienna (Journ. d'Erdmann, Mars, 1844), and by Faraday. According to the latter the temperature required is 148° F., by which it is converted into a colorless crystalline solid.—R. B.

† See p. 93.

‡ M. Natterrer, it is stated, has also liquefied and solidified the deutoxide of nitrogen, but by a pressure of 50 atmospheres and the temperature of 166° F., Faraday was unable to produce any signs of liquefaction.—R. B.

cold is colorless, but becomes green at the ordinary temperature of the air. Its vapor is orange red.

Hyponitrous acid is decomposed by water, being converted into nitric acid and binoxide of nitrogen. For this reason, it cannot be made to unite directly with metallic oxides; hyponitrite of lead may, however, be prepared by digesting metallic lead in a solution of the nitrate, and many other salts by indirect means.

Nitrous acid.—The term *acid* applied to this substance is hardly correct, since it does not seem to possess the power of forming salts; the expression has notwithstanding been long sanctioned by use. It is the vapor of nitrous acid which forms the deep red fumes always produced when binoxide of nitrogen escapes into the air.

When carefully dried nitrate of lead is exposed to heat in a retort of hard glass, it is decomposed; oxide of lead remains behind, while the acid is resolved into a mixture of oxygen and nitrous acid. By surrounding the receiver with a very powerful freezing mixture, the latter is condensed to the liquid form. It is then nearly colorless, but acquires a yellow, and ultimately a red tint, as the temperature rises. At 82° it boils, giving off its well-known red vapor, the intensity of the color of which is greatly augmented by elevation of temperature.

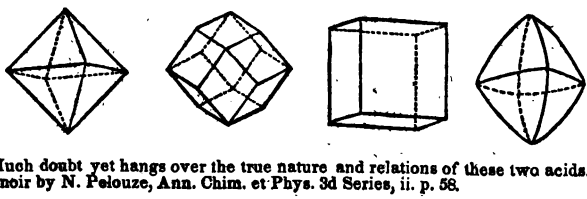
This substance, like the preceding, is decomposed by water, being resolved into deutoxide of nitrogen and nitric acid. Its vapor is absorbed by strong nitric acid, which thereby acquires a yellow or red tint, passing into green, then into blue, and afterwards disappearing altogether, on the addition of successive portions of water. The deep red fuming acid of commerce called *nitrous* acid, is simply nitric acid impregnated with nitrous gas.*

CARBON.

This substance occurs in a state of purity, and crystallized, in two distinct and very dissimilar forms, namely as diamond, and as graphite or plumbago. It constitutes a large proportion of all organic structures, animal and vegetable: when these latter are exposed to destructive distillation in close vessels, a great part of this carbon remains, associated with the earthy and alkaline matter of the tissue, giving rise to the many varieties of charcoal, coke, &c.

The diamond is one of the most remarkable substances known; long prized on account of its brilliancy as an ornamental gem, the discovery of its curious chemical nature confers upon it a high degree of scientific interest. Several localities in India, the Island of Borneo, and more especially Brazil, furnish this beautiful substance. It is always distinctly crystallized, often quite transparent and colorless, but now and then having a shade of yellow, pink, or blue. The origin and true geological position of the diamond are unknown; it is always found imbedded in gravel and transported materials whose history cannot be traced. The crystalline form of the diamond is that of the regular

Fig. 92.



* Much doubt yet hangs over the true nature and relations of these two acids.—See a Memoir by N. Pelouze, Ann. Chim. et Phys. 3d Series, ii. p. 58.

octahedron or cube, or some figure geometrically connected with these; many of the octahedral crystals exhibit a very peculiar appearance, arising from the faces being curved or rounded, which gives to the crystal an almost spherical figure.

The diamond is infusible and inalterable by a very intense heat, provided air be excluded; heated to ordinary redness in a vessel of oxygen, it burns with facility, yielding carbonic acid gas.

This is the hardest substance known; it admits of being split or cleaved without difficulty in certain particular directions, but can only be cut or abraded by a second portion of the same material; the powder rubbed off in this process serves for polishing the new faces, and is also highly useful to the lapidary and seal-engraver. One very curious and useful application of the diamond is made by the glazier; a *fragment* of this mineral, like a bit of flint or any other hard substance, scratches the surface of glass; a *crystal* of diamond having the rounded octahedral figure spoken of, held in one particular position on the glass, namely, with an edge formed by the meeting of two adjacent faces presented to the surface, and then drawn along with gentle pressure, causes a deep split or cut, which penetrates to a considerable depth into the glass and determines its fracture with perfect certainty.

Graphite or plumbago, appears to consist essentially of pure carbon, although most specimens contain iron, the quantity of which varies from a mere trace, up to five per cent. Graphite is a somewhat rare mineral; the finest, and most valuable for pencils, is brought from Borrowdale, in Cumberland, where a kind of irregular vein is found traversing the ancient slate beds of that district. Crystals are not common; when they occur, they have the figure of a short six-sided prism;—a form bearing no geometric relation to that of the diamond.

Graphite is often formed artificially in certain metallurgic operations; the brilliant scales which sometimes separate from melted cast-iron on cooling, called by the workmen "kish," consist of graphite.

Lamp-black, the soot produced by the imperfect combustion of oil or resin, is the best example that can be given of pure carbon in its uncrystallized or *amorphous* state. To the same class belong the different kinds of charcoal. That prepared from wood, either by distillation in a large iron retort, or by the smothered combustion of a pile of fagots partially covered with earth, is the most valuable as fuel. Coke, the charcoal of pit-coal, is much more impure; it contains a large quantity of earthy matter, and very often sulphur; the quality depending very much upon the mode of preparation. Charcoal from bones and animal matters in general, is a very valuable substance on account of the extraordinary power it possesses of removing coloring matters from organic solutions; it is used for this purpose by the sugar-refiners to a very great extent, and also by the manufacturing and scientific chemist. The property in question is possessed by all kinds of charcoal in a small degree.

Charcoal made from box, or other dense wood, has the property of condensing into its pores gases and vapors; of ammoniacal gas it is said to absorb no less than 90 times its volume, while of hydrogen it takes up less than twice its own bulk, the quantity being apparently connected with the property in the gas of suffering liquefaction. This effect, as well as that of the decolorizing power, no doubt depends in some way upon the same peculiar action of surface so remarkable in the case of platinum in a mixture of oxygen and hydrogen.*

* Carbon is a combustible uniting with oxygen and producing carbonic acid. Its different forms exhibit much difference in this respect; in the very porous condition of charcoal it burns readily, while in its most dense form, the diamond, it requires a bright

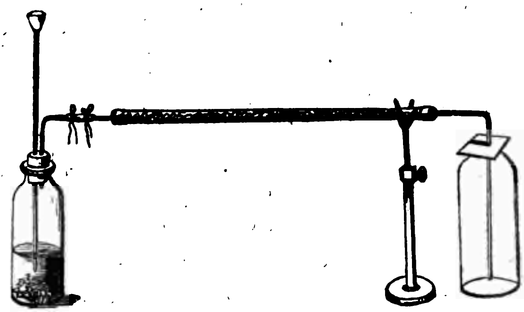
Compounds of Carbon and Oxygen.

There are two direct compounds of carbon and oxygen, called carbonic oxide and carbonic acid; their composition may be thus stated:—

	Composition by weight.	
	Carbon.	Oxygen.
Carbonic oxide	6	8
Carbonic acid	6	16

Carbonic acid is always produced when charcoal burns in air or oxygen gas; it is most conveniently obtained, however, for study by decomposing a carbonate with one of the stronger acids. For this purpose, the apparatus for generating hydrogen may again be employed; fragments of marble are put into the bottle with enough water to cover the extremity of the funnel-tube, and hydrochloric or nitric acid added by the latter, until the gas is freely disengaged. Chalk-powder, and dilute sulphuric acid may be used instead. The gas may be collected over water, although with some loss; or very conveniently, by displacement, if it be required dry, as shown in the figure. The long drying tube is filled with fragments of chloride of calcium, and the heavy gas is conducted to the bottom of the vessel in which it is to be received, the mouth of the latter being lightly closed.*

Fig. 93.



Carbonic acid gas is colorless; it has an agreeable pungent taste and odor, but cannot be respired for a moment wihout insensibility following. Its specific gravity is 1·524,† 100 cubic inches weighing 47·26 grains.

red heat and pure oxygen gas. In the form of charcoal it conducts heat slowly and electricity readily. Carbon is insoluble in water and not liable to be affected by air and moisture. It retards putrefaction.—R. B.

* In connecting tube apparatus for conveying gases or cold liquids, not corrosive, little tubes of caoutchouc, about an inch long, are *inexpressibly* useful. These are made by bending a piece of sheet India-rubber loosely round a glass tube or rod, and cutting off the superfluous portion with sharp scissors. The fresh cut edges of the caoutchouc, pressed strongly together, cohere completely, and the tube is perfect, provided they have not been soiled by touching with the fingers. The connecters are secured by two or three turns of thin silk cord. The glass tubes are sold by weight, and are easily bent in the flame of a spirit-lamp, and, when necessary, cut by scratching with a file, and breaking asunder.

Fig. 94.

† MM. Dulong and Berzelius.

This gas is very hurtful to animal life, even when largely diluted with air; it acts as a narcotic poison. Hence the danger arising from imperfect ventilation, the use of fire-places and stoves of all kinds unprovided with proper chimneys, and the crowding together of many individuals in houses and ships without efficient means for renewing the air. Carbonic acid is sometimes emitted in large quantity from the earth in volcanic districts, and it is constantly generated where organic matter is in the act of undergoing fermentive decomposition. The fatal "after-damp" of the coal-mines contains a large proportion of carbonic acid.

A lighted taper plunged into carbonic acid is instantly extinguished, even to the red-hot snuff. When diluted with three times its volume of air, it still has the power of extinguishing a light. The gas is easily known from nitrogen, which is also incapable of supporting combustion, by its rapid absorption by caustic alkali, or by lime water; the turbidity communicated to the latter from the production of insoluble carbonate of lime is very characteristic.

Cold water dissolves about its own volume of carbonic acid, whatever be the density of the gas with which it is in contact; the solution temporarily reddens litmus paper. In common soda-water, and also in effervescent wines, examples may be seen of this solubility of the gas.

Some of the interesting phenomena attending the liquefaction of carbonic acid have been already described; it requires for the purpose a pressure of between 27 and 28 atmospheres at 32°, according to Mr. Addams. The liquefied acid is colorless and limpid, lighter than water, and four times more expansible than air; it mixes in all proportions with ether, alcohol, naphtha, oil of turpentine, and bisulphuret of carbon, and is insoluble in water and fat oils.* It is probably destitute when in this condition of all properties of an acid.†

Carbonic acid exists, as already mentioned, in the air; relatively, its quantity is but small, but absolutely, taking into account the vast extent of the atmosphere, it is very great, and fully adequate to the purpose for which it is designed, namely, to supply to plants their carbon, these latter having the power by the aid of their green leaves, of decomposing carbonic acid, retaining the carbon, and expelling the oxygen. The presence of light is essential to this extraordinary effect, but of the manner of its execution we are yet ignorant.

The carbonates form a very large and important group of salts, some of which occur in nature in great quantities, as the carbonates of lime and magnesia.

Carbonic oxide.—When carbonic acid is passed over red-hot charcoal or metallic iron, one-half of its oxygen is removed, and it becomes converted into carbonic oxide. A very good method of preparing this gas is to introduce into a flask fitted with a bent tube some crystallized oxalic acid, or salt of sorrel, and pour upon it five or six times as much strong oil of vitriol. On heating the mixture the organic acid is resolved into water, carbonic acid and carbonic oxide; by passing the gases through a strong solution of caustic potash, the first is withdrawn by absorption, while the second remains unchanged. Another, and it may be preferable method, is to heat finely-powdered yellow ferrocyanide of potassium with eight or ten times its weight of concentrated sulphuric acid. The salt is entirely decomposed, yielding a

* Graham, Elements, p. 305.

† When relieved of pressure it immediately boils, and seven parts out of eight assume the gaseous state, the rest becoming solid at 90° F. (Mitchell). Solid carbonic acid mixed with ether produces in vacuo a very intense cold (165° F. Faraday) capable of solidifying many gases when aided by pressure. Liquid carbonic acid immersed in this mixture, becomes a solid so clear and transparent, that its condition cannot be detected until a portion again becomes liquid.—R. B.

most copious supply of perfectly pure carbonic oxide gas, which may be collected over water in the usual manner.*

Carbonic oxide is a combustible gas; it burns with a beautiful pale blue flame, generating carbonic acid. It has never been liquefied. It is colorless, has very little odour, and is extremely poisonous, even worse than carbonic acid. Mixed with oxygen, it explodes by the electric spark, but with some difficulty. Its specific gravity is ·973; 100 cubic inches weigh 30·21 grains.

The relation by volume of these oxides of carbon may thus be made intelligible:—carbonic acid contains its own volume of oxygen, that gas suffering no change of bulk by its conversion. One measure of carbonic oxide mixed with half a measure of oxygen and exploded, yields one measure of carbonic acid; hence carbonic oxide contains half its volume of oxygen.

Carbonic oxide unites with chlorine under the influence of light, forming a pungent, suffocating compound, possessing acid properties, called phosgene gas, or chloro-carbonic acid. It is made by mixing equal volumes of carbonic oxide and chlorine, both perfectly dry, and exposing the mixture to sunshine; the gases unite quietly, the color disappears, and the volume becomes reduced to one-half. It is decomposed by water.

SULPHUR.

This is an elementary body of great importance and interest. Sulphur is often found in a free state in connection with deposits of gypsum and rock-salt; its occurrence in volcanic districts is probably accidental. Sicily furnishes a large proportion of the sulphur employed in Europe. In a state of combination with iron and other metals, and as sulphuric acid, united to lime and magnesia, it is also abundant.

Pure sulphur is a pale yellow brittle solid, of well known appearance. Its specific gravity is 1·98; it melts when heated, and distils over unaltered, if air be excluded. The crystals of sulphur exhibit two distinct and incompatible forms, namely, an octahedron with rhombic base, which is the figure assumed when sulphur separates from solution at common temperatures, and a length-

Fig. 95.

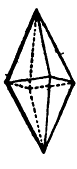
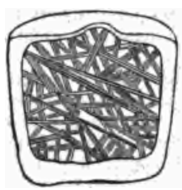


Fig. 96.



ened prism, having no relation to the preceding; this happens when a mass of sulphur is melted, and after partial cooling, the crust at the surface broken, and the fluid portion poured out. Fig. 96 shows the result of such an experiment.

Sulphur melts at 232° Fahrenheit; at this temperature it is of the color of amber, and thin and fluid as water, when further heated, it begins to thicken, and to acquire a deeper color; and between 430° and 480° it is so tenacious that the vessel in which it is contained may be inverted for a moment without the loss of its contents. From the temperature last mentioned to the boiling point, about 600°, it again becomes thinner. In the preparation of

* See a paper by the author in Memoirs of Chem. Soc. of London, i. p. 261.

commercial flowers of sulphur the vapor is conducted into a large cold chamber, where it condenses in minute crystals. The specific gravity of sulphur vapor is 6·654.

Sulphur is insoluble in water and alcohol; oil of turpentine and the fat oils dissolve it, but the best substance for the purpose is bisulphuret of carbon. In its chemical relations, sulphur bears great resemblance to oxygen; to very many oxides there are corresponding sulphurets, and these sulphurets often unite among themselves, forming crystallizable compounds analogous to salts.

Compounds of Sulphur and Oxygen.

	Composition by weight.	
	Sulphur.	Oxygen.
Sulphurous acid	16·09	16
Sulphuric acid*	16·09	24
Hyposulphurous acid	32·18	16
Hyposulphuric acid	32·18	40
Sulphuretted-hyposulphuric acid	48·27	40
Bisulphuretted-hyposulphuric acid†	64·36	40

Sulphurous acid.—This is the only product of the combustion of sulphur in dry air or oxygen gas. It is most conveniently prepared by heating oil of vitriol with metallic mercury or copper clippings; a portion of the acid is decomposed, one-third of its oxygen being transferred to the metal, while the sulphuric acid becomes sulphurous. Sulphurous acid thus obtained is a colorless gas, having the peculiar suffocating odour of burning brimstone; it instantly extinguishes flame; and is quite irrespirable. Its density is 2·21, 100 cubic inches weighing 68·69 grains. At 0° F. under the pressure of the atmosphere, this gas condenses to a colorless, limpid liquid, very expansible by heat.‡ Cold water dissolves more than thirty times its volume of sulphurous acid. The solution may be kept unchanged so long as air is excluded, but access of oxygen gradually converts the sulphurous into sulphuric acid, in the presence of water although the dry gases may remain in contact for any length of time without change.

One volume of sulphurous acid gas contains one volume of oxygen and $\frac{1}{6}$th of a volume of sulphur vapor, condensed into one volume.

Gases which, like the present, are freely soluble in water, must be collected by displacement, or by the use of the mercurial pneumatic trough. The manipulation with the latter is exactly the same in principle as with the ordinary water-trough, but rather more troublesome, from the great density of the mercury, and its opacity. The whole apparatus is on a much smaller scale. The

* The terminations *ous* and *ic*, applied to acids, signify degrees of oxydation, the latter being the highest; acids ending in *ous* form salts the names of which are made to end in *ite*, and those in *ic* terminate in *ate*, as *sulphurous* acid, *sulphite* of soda; *sulphuric* acid, *sulphate* of soda.

† The more advanced student will be glad to see these stated in equivalents by the use of symbols, hereafter to be explained, their relations becoming thereby much more evident. The numbers given are really the equivalent numbers, but are intended only to show the proportions of sulphur and oxygen, without any reference to other bodies. The following are the quantities required to saturate one equivalent of a base:—

Sulphurous acid	SO_2
Sulphuric acid	SO_3
Hyposulphurous acid	S_2O_2
Hyposulphuric acid	S_2O_5
Sulphuretted hyposulphuric acid	S_3O_5
Bisulphuretted-hyposulphuric acid	S_4O_5

‡ Liquid sulphurous acid freezes at 105° F. into a colorless transparent solid (Faraday). The gas itself when moist is rendered solid by cold, a hydrate being formed containing about 20 per cent. of water.—R. B.

trough is best constructed of hard, sound wood, and so contrived as to economize as much as possible the expensive fluid it is to contain.

Sulphurous acid has bleaching properties; it is used in the arts for bleaching woollen goods and straw-plait. A piece of blue litmus paper plunged into the moist gas is first reddened and then slowly bleached.*

The salts of sulphurous acid are not of much importance; those of the alkalis are soluble and crystallizable; they are easily formed by direct combination. Sulphites of baryta, strontia, and lime are insoluble in water, but soluble in hydrochloric acid. The strong acids decompose them; nitric acid converts them into sulphates.

Sulphuric acid.—Hydrated sulphuric acid has been known since the fifteenth century. There are two distinct processes by which it is at the present time prepared, namely, by the distillation of green sulphate of iron, and by the oxidation of sulphurous acid by nitrous acid.

The first process is still carried on at Nordhausen in Saxony; the sulphate of iron, derived from the oxidation of iron pyrites, is deprived by heat of the greater part of its water of crystallization, and subjected to a high red heat in earthen retorts, to which receivers are fitted as soon as the acid begins to distil over. A part gets decomposed by the very high temperature; the remainder is driven off in vapor, which is condensed by the cold vessels. The product is a brown oily liquid, of about 1·9 specific gravity, fuming in the air, and very corrosive. It is chiefly made for the purpose of dissolving indigo.

The second method, which is perhaps, with the single exception mentioned, always followed as the more economical, depends upon the fact that when sulphurous acid, nitrous acid, and water are present in certain proportions, the sulphurous acid becomes oxidized at the expense of the nitrous acid, which by the loss of one-half of its oxygen sinks to the condition of deutoxide of nitrogen. The operation is thus conducted:—A large and very long chamber is built of sheet-lead supported by timber framing; on the outside at one extremity a small furnace or oven is constructed, having a wide tube leading into the chamber. In this sulphur is kept burning, the flame of which heats a crucible containing a mixture of nitre and oil of vitriol. A shallow stratum of water occupies the floor of the chamber, and sometimes a jet of steam is also introduced. Lastly, an exit is provided at the remote end of the chamber for the spent and useless gases. The effect of these arrangements is to cause a constant supply of sulphurous acid, atmospheric air, nitric acid vapor, and water in the state of steam, to be thrown into the chamber, there to mix and react upon each other. The nitric acid immediately gives up a part of its oxygen to the sulphurous acid, becoming nitrous; it does not remain in this state, however, but suffers further de-oxidation until it becomes reduced to deutoxide of nitrogen. That substance in contact with free oxygen, absorbs a portion of the latter, and once more becomes nitrous acid, which is again destined to undergo de-oxidation by a fresh quantity of sulphurous acid. A very small portion of nitrous acid, mixed with atmospheric air and sulphurous acid, may thus in time convert an indefinite amount of the latter into sulphuric acid, by acting as a kind of carrier between the oxygen of the air and the sulphurous acid. The presence of water is essential to this reaction:—

We may thus represent the change.

Nitrous acid 46·06	Nitrogen	14·06	Deutoxide of nitrogen 30·06
	Oxygen	16	
	Oxygen	16	
Sulphurous acid 64·18	Sulphur	32·18	
	Oxygen	32	
Water . . .		18	Hydrated sulphuric acid 98·18

* It does not bleach by destroying the coloring matter, but by forming with it a color-

Such is the simplest view that can be taken of the production of sulphuric acid in the leaden chamber, but it is too much to affirm that it is strictly true; it may be more complex. When a little water is put at the bottom of a large glass globe so as to maintain a certain degree of humidity in the air within, and sulphurous and nitrous acids are introduced by separate tubes, symptoms of chemical action become immediately evident, and after a little time, a white crystalline matter is observed to condense on the sides of the vessel. This substance appears to be a compound of sulphuric acid, hyponitrous acid and a little water.* When thrown into water, it is resolved into sulphuric acid, deutoxide of nitrogen, and nitric acid. This curious body is certainly very often produced in large quantity in the leaden chambers, but that its production is indispensable to the success of the process, and constant when the operation goes on well and the nitrous acid is not in excess, may perhaps admit of doubt.

The water at the bottom of the chamber thus becomes loaded with sulphuric acid; when a certain degree of strength has been reached, it is drawn off and concentrated by evaporation, first in leaden pans, and afterwards in stills of platinum, until it attains a density (when cold) of 1·84, or thereabouts; it is then transferred to carboys, or large glass bottles fitted in baskets, for sale. In Great Britain this manufacture is one of great national importance, and is carried on to a vast extent. An inferior kind of acid is now made by burning iron pyrites, or poor copper ore, as a substitute for Sicilian sulphur; this is chiefly used by the makers for their own consumption; it very frequently contains arsenic.

The most concentrated sulphuric acid, or *oil of vitriol*, as it is often called, is a definite combination of 40·09 parts real acid, and 9 parts water. It is a colorless, oily liquid, having a specific gravity of about 1·85, of intensely acid taste and reaction. Organic matter is rapidly charred and destroyed by this substance. At the temperature of —15°, it freezes, and 620°, it boils, and may be distilled without decomposition. Oil of vitriol has a most energetic attraction for water; it withdraws aqueous vapors from the air, and when diluted, great heat is evolved, so that the mixture always requires to be made with caution. Oil of vitriol is not the only hydrate of sulphuric acid; three others are known to exist. When the fuming oil of vitriol of Nordhausen is exposed to a low temperature, a white crystaline substance separates, which is a hydrate containing half as much water as the common liquid acid. Then again, a mixture of 49 parts strong liquid acid, and 9 parts water, congeals or crystallizes at a temperature above 32°, and remains solid even at 45°. Lastly, when a very dilute acid is concentrated by evaporation in vacuo over surface of oil of vitriol, the evaporation stops when the real acid and water bear to each other the proportion of 40·09 to 27.

When good Nordhausen oil of vitriol is exposed in a retort to a gentle heat and a receiver cooled by a freezing mixture fitted to it, a volatile substance distils over in great abundance, which condenses into beautiful, white, silky,

less combination, hence the color is restored on neutralizing the sulphurous acid by an alkali.—R. B.

* M. Gaultier de Claubry assigned to this curious substance the composition expressed by the formula $4HO, 2NO_3 + 5SO_3$. and this view has generally been received by recent chemical writers. M. de la Provostaye has since shown that a compound, possessing all the essential properties of the body in question may be formed by bringing together, in a sealed glass tube, liquid sulphurous acid and liquid nitrous acid, both free from water. The white crystalline solid soon begins to form, and at the expiration of twenty-six hours the reaction appears complete The new product is accompanied by an exceedingly volatile greenish liquid, having the characters of hyponitrous acid. The white substance, on analysis, was found to contain the elements of two equivalents of sulphuric acid and one of hyponitrous acid. or $NO_3, + 2SO_3$. M. de la Provostaye very ingeniously explains the anomalies in the different analyses of the leaden chamber product, by showing that the pure substance forms crystallizable combinations with different proportions of liquid sulphuric acid. (Ann. Chim. et Phys., lxxiii. p. 362.)

crystals resembling those of asbestos; this bears the name of anhydrous sulphuric acid. When put into water it hisses like a hot iron, from the violence with which combination occurs; exposed to the air even for a few moments, it liquefies by absorption of moisture, forming common liquid sulphuric acid. It forms an exceedingly curious compound with dry ammoniacal gas, quite distinct from ordinary sulphate of ammonia, and which, indeed, possesses none of the characters of a sulphate. It is doubtful whether this interesting substance is to be looked upon as identical with the acid of the sulphates; the latter may perhaps be, like nitric acid and a great number of others, incapable of existing in a separate state.

Sulphuric acid, in all soluble states of combination, may be detected with the greatest ease by solution of nitrate of barytes, or chloride of barium. A white precipitate is produced which does not dissolve in nitric acid.

Hyposulphurous acid.—By digesting sulphur with a solution of sulphite of potash or soda, a portion of that substance is dissolved, and the liquid, by slow evaporation, furnishes crystals of the new salt. The acid cannot be isolated; when hydrochloric acid is added to a solution of a hyposulphite, the acid of the latter is instantly resolved into sulphur, which precipitates, and into sulphurous acid, easily recognized by its odor. The most remarkable feature of the alkaline hyposulphites, is their property of dissolving certain insoluble salts of silver, as the chloride;—a property which has lately conferred upon them a considerable share of importance in relation to the art of photogenic drawing.

Hyposulphuric acid.—This is prepared by suspending finely divided peroxide of manganese in water artificially cooled, and then transmitting a stream of sulphurous acid gas; the peroxide becomes protoxide, half its oxygen converting the sulphurous acid into hyposulphuric. The hyposulphate of manganese thus prepared, is decomposed by a solution of pure hydrate of barytes, and the barytic salt, in turn, by enough sulphuric acid to precipitate the base. The solution of hyposulphuric acid may be concentrated by evaporation in vacuo, until it acquires a density of 1·347; pushed further, it decomposes into sulphuric and sulphurous acids. It has no odor, is very sour, and forms soluble salts with baryta, lime, and oxide of lead.

Sulphuretted-hyposulphuric acid.—A substance accidentally formed by M. Langlois,* in the preparation of hyposulphite of potash, by gently heating with sulphur, a solution of carbonate of potash, previously saturated with sulphurous acid. The salts bear a great resemblance to those of hyposulphurous acid, but differ completely in composition, while the acid itself is not quite so prone to change

Bisulphuretted-hyposulphuric acid.—This was discovered by MM. Fordos and Gélis.† When iodine is added to a solution of hyposulphite of soda, a large quantity of that substance is dissolved, and a clear colorless solution obtained, which, besides iodide of sodium, contains a salt of a peculiar acid, richer in sulphur than the preceding. By suitable means, the new substance can be eliminated, and obtained in a state of solution. It very closely resembles hyposulphuric acid.

Sulphurous acid unites, under peculiar circumstances, with chlorine, and also with iodine, forming compounds, which have been called chloro and iodosulphuric acids. They are decomposed by water. It also combines with dry ammoniacal gas, giving rise to a remarkable compound, and with nitric oxide also, in presence of an alkali.

* Ann. Chim. et Phys., 3d series, iv. p. 77.
† Ib., vi. p. 454.

SELENIUM.

This is a very rare substance, much resembling sulphur in its chemical relations, and found in association with that element in some few localities, or replacing it in certain metallic combinations, as in the seleniuret of lead of Clausthal in the Hartz.

Selenium is a reddish-brown solid body, somewhat translucent, and having an imperfect metallic lustre. Its specific gravity is 4·3. At 212°, or a little above, it melts, and at 650° boils. It is insoluble in water, and exhales, when heated in the air, a peculiar and disagreeable odor, which has been compared to that of decaying horse-radish. There are three oxides of selenium, two of which correspond respectively to sulphurous and sulphuric acids, while the third has no known analogue in the sulphur series.

	Composition by weight.	
	Selenium.	Oxygen.
Oxide of Selenium	39·57	8
Selenious acid	39·57	16
Selenic acid	39·57	24

Oxide.—Formed by heating selenium in the air.—It is a colorless gas, slightly soluble in water, and has the remarkable odor above described. It has no acid properties.

Selenious acid.—This is obtained by dissolving selenium in nitric acid, and evaporating to dryness. It is a white, soluble, deliquescent substance, of distinct acid properties, and may be sublimed without decomposition. Sulphurous acid decomposes it, precipitating the selenium.

Selenic acid.—Prepared by fusing nitrate of potash or soda, with selenium, precipitating the seleniate so produced by a salt of lead, and then decomposing the compound by sulphuretted hydrogen. The hydrated acid strongly resembles oil of vitriol; but, when very much concentrated, decomposes by the application of heat, into selenious acid and oxygen. The seleniates bear the closest analogy to the sulphates in every particular.

PHOSPHORUS.

Phosphorus in the state of phosphoric acid, is contained in the ancient unstratified rocks, and in the lavas of modern origin. As these disintegrate, and crumble down into fertile soil, the phosphates pass into the organism of plants, and ultimately into the bodies of the animals to which these latter serve for food. The earthy phosphates play a very important part in the structure of the animal frame by communicating stiffness and inflexibility to the bony skeleton.

This element was discovered in 1669, by Brandt of Hamburg, who prepared it from urine. The following is an outline of the process now adopted. Thoroughly calcined bones are reduced to powder, and mixed with two-thirds of their weight of sulphuric acid, diluted with a considerable quantity of water; this mixture, after standing some hours, is filtered, and the nearly insoluble sulphate of lime washed. The liquid is then evaporated to a syrupy consistence, mixed with charcoal powder, and the desiccation completed in an iron vessel, exposed to a high temperature. When quite dry, it is transferred to a stone-ware retort, to which a wide bent tube is luted, dipping a little way into the water contained in the receiver. A narrow tube serves to

Fig. 97.

give issue to the gases, which are conveyed to a chimney. This manufacture is now conducted on a very great scale, the consumption of phosphorus for the apparently trifling article of instantaneous light matches, being something prodigious.

Phosphorus, when pure, very much resembles in appearance, imperfectly bleached wax, and is soft and flexible at common temperatures. Its density is 1·77, and that of its vapor 4·35, air being unity. At 108° it melts, and at 550° boils. It is insoluble in water, and is usually kept immersed in that liquid, but dissolves in oils and in native naphtha. When set on fire in the air, it burns with a bright flame, generating phosphoric acid. Phosphorus is exceedingly inflammable; it sometimes takes fire by the heat of the hand and demands great care in its management; a blow or hard rub will very often kindle it. A stick of phosphorus held in the air always appears to emit a whitish smoke, which in the dark is luminous. This effect is due to a slow combustion which the phosphorus undergoes by the oxygen of the air, and upon it depends one of the methods employed for the analysis of the atmosphere, as already described. It is singular that the slow oxidation of phosphorus may be entirely prevented by the presence of a small quantity of olefiant gas, or the vapor of ether, or some essential oil; it may even be distilled in an atmosphere containing vapor of oil of turpentine in considerable quantity. Neither does the action go on in pure oxygen, at least at the temperature of 60°, which is very remarkable, but if the gas be rarefied, or diluted with nitrogen, hydrogen, or carbonic acid, oxidation is set up.

Compounds of phosphorus and oxygen.—These are four in number, and have the composition below indicated.

	Composition by weight.	
	Phosphorus.	Oxygen.
Oxide of phosphorus	62·76	8
Hypophosphorous acid	31·38	8
Phosphorous acid	31·38	24
Phosphoric acid*	31·38	40

Oxide of phosphorus.—When phosphorus is melted beneath the surface of hot water, and a stream of oxygen gas forced upon it from a bladder, combustion ensues, and the phosphorus is converted in great part into a brick-red powder, which is the substance in question in a very impure state.

A better method is to introduce into a large wide-necked flask, a quantity of phosphorus cut into small pieces, with enough chloride of phosphorus to cover it, and leave the whole exposed to the air for twenty-four hours. Phosphoric acid and oxide of phosphorus are slowly formed, and enter into a kind of combination. The excess of chloride being decanted, the solid matter is detached from the flask and put into water, in which the compound dissolves. By heating this solution to 176° it is decomposed, and the oxide precipitates

* In symbols—

Oxide of phosphorus	P_2O
Hypophosphorous acid	PO
Phosphorous acid	PO_3
Phosphoric acid	PO_5

Equivalent of phosphorus, 31·38.

in the state of hydrate; which may be collected on a filter, and dried over oil of vitriol.

The pure oxide is a red or yellow powder, according to its state of division. It is decomposed by heat into phosphorus and phosphoric acid.*

Hypophosphorous acid.—When phosphuret of barium is put into water, that liquid is decomposed, giving rise to phosphuretted hydrogen, phosphoric acid, hypophosphorous acid, and baryta; the first escapes as gas, and the two acids remain in union with the baryta. By filtration the soluble hypophosphite is separated from the insoluble phosphate. On adding to the liquid the quantity of sulphuric acid necessary to precipitate the base, the hypophosphorous acid is obtained in solution. By evaporation it may be reduced to a syrupy consistence.

The acid is a powerful de-oxidizing agent. All its salts are soluble in water.

Phosphorous acid.—Phosphorous acid is formed by the slow combustion of phosphorus in the atmosphere; or by burning that substance by means of a very limited supply of air, in which case it is anhydrous, and presents the aspect of a white powder. The hydrated acid is more conveniently prepared by adding water to the chloride of phosphorus, when mutual decomposition takes place, the oxygen of the water being transferred to the phosphorus, generating phosphorous acid, and its hydrogen to the chlorine, giving rise to hydrochloric acid. By evaporating the solution to the consistence of syrup, the hydrochloric acid is expelled, and the residue on cooling crystalizes.

Hydrated phosphorous acid is very deliquescent, and very prone to attract oxygen and pass into phosphoric acid. When heated in a close vessel, it is resolved into hydrated phosphoric acid and pure phosphuretted hydrogen gas. It is composed of 55·38 parts real acid and 27 parts water.†

The phosphites are of little importance.

Phosphoric acid.—When phosphorus is burned under a bell-jar by the aid of a copious supply of dry air, snow-like anhydrous phosphoric acid is produced in great quantity. This substance exhibits as much attraction for water as anhydrous sulphuric acid; exposed to the air for a few moments, it deliquesces to a liquid, and when thrown into water, combines with the latter with explosive violence. Once in the state of hydrate, the water cannot again be separated.

When nitric acid of moderate strength is heated in a retort to which a receiver is connected, and fragments of phosphorus added singly, taking care to suffer the violence of the action to subside between each addition, the phosphorus is oxidized to its maximum and converted into phosphoric acid. By distilling off the greater part of the acid, transferring the residue in the retort to a platinum vessel, and then cautiously raising the heat to redness, the hydrated acid may be obtained pure. This is the *glacial phosphoric acid* of the Pharmacopœia.

A third method consists in taking the acid phosphate of lime produced by the action of sulphuric acid on bone-earth, precipitating it with a slight excess of carbonate of ammonia, separating by a filter the insoluble lime salt, and then evaporating and igniting in a platinum vessel the mixed phosphate and sulphate of ammonia. Hydrated phosphoric acid alone remains behind. It is exceedingly deliquescent, and requires to be kept in a closely stopped bottle. The glacial acid contains 71·38 parts real acid and 9 parts water.

Phosphoric acid is a powerful acid; its solution has an intensely sour taste, and reddens litmus paper; it is not poisonous.

There are few bodies that present a greater degree of interest to the che-

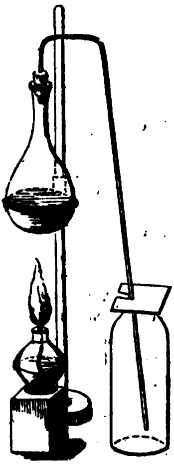
* Leverrier, Ann. Chim. et Phys., lxv. p. 257.

† Or, $3HO+PO_3$.

mist than this substance; the extraordinary changes its compounds undergo by the action of heat, chiefly made known to us by the admirable researches of Mr. Graham, will be found described in connection with the general history of saline compounds.

CHLORINE.

Fig. 98.



This substance is a member of a small natural group containing besides, iodine, bromine, and fluorine. So great a degree of resemblance exists between these bodies in all their chemical relations, that the history of one will almost serve, with a few little alterations, for that of the rest.

Chlorine* is a very abundant substance; in common salt it exists in combination with sodium. It is most easily prepared by pouring strong liquid hydrochloric acid upon finely-powdered black oxide of manganese, contained in a retort or flask, and applying a gentle heat; a heavy yellow gas is disengaged, which is the substance in question.

It may be collected over warm water, or by displacement—the mercurial trough cannot be employed, as the chlorine rapidly acts upon the metal, and becomes absorbed.

The reaction is very easily explained. Hydrochloric acid is a compound of chlorine and hydrogen; when this is mixed with a metallic protoxide, double interchange of elements takes place, water and chloride of the metal being produced. But when a *peroxide*, containing twice as much oxygen as the protoxide, is substituted, an additional effect ensues, namely, the decomposition of a second portion of hydrochloric acid by the oxygen in excess, the hydrogen of which is withdrawn and the chlorime set free.

Hydrochloric acid	Chlorine	Chlorine.
	Hydrogen	Water.
Peroxide of manganese	Oxygen	
	Manganese	Chloride of manganese.
	Oxygen	
Hydrochloric acid	Chlorine	
	Hydrogen	Water.

Chlorine was discovered in 1774, by Scheele, but its nature was long misunderstood. It is a yellow gaseous body, of intolerably suffocating properties, producing very violent cough and irritation when inhaled to an exceedingly small extent. It is somewhat soluble in water, that liquid absorbing at 60° about twice its volume, and acquiring the color and odor of the gas. When this solution is exposed to light, it is slowly changed by decomposition of water into hydrochloric acid, the oxygen being at the same time liberated. When moist chlorine gas is exposed to a cold of 32°, yellow crystals are formed, which consist of a definite compound of chlorine and water, containing 35·4 parts of the former to 90 of the latter.

Chlorine has a specific gravity of 2·47, 100 cubic inches weighing 76·6

* From χλωρός, yellowish-green, the name given to it by Sir H. Davy.

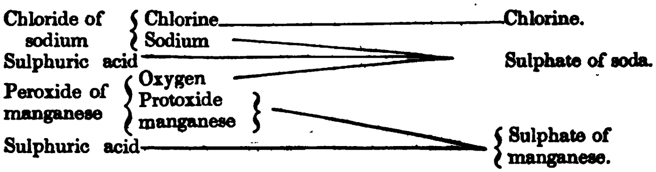
grains. Exposed to a pressure of about four atmospheres, it condenses to a yellow limpid liquid.

This substance has but little attraction for oxygen, its chemical energies being principally exerted towards hydrogen and the metals. When a lighted taper is plunged into the gas, it continues to burn with a dull red light, and emits a large quantity of smoke, the hydrogen of the wax being alone consumed, and the carbon separated. If a piece of paper be wetted with oil of turpentine and thrust into a bottle filled with chlorine, the chemical action of the latter upon the hydrogen is so violent as to cause inflammation, accompanied by a copious deposit of soot. Although chlorine can, by indirect means, be made to combine with carbon, yet this never occurs under the circumstances described.

Phosphorus takes fire spontaneously in chlorine; it burns with a pale and feebly luminous flame. Several of the metals, as copper leaf, powdered antimony and arsenic, undergo combustion in the same manner. A mixture of equal measures chlorine and hydrogen explodes with violence on the passage of an electric spark, or on the application of a lighted taper, hydrochloric acid gas being formed. Such a mixture may be retained in the dark for any length of time without change; exposed to diffuse day-light, the two gases slowly unite, while the direct rays of the sun induce instantaneous explosion.

The most characteristic property of chlorine is its bleaching power; the most stable organic coloring principles are instantly decomposed and destroyed by this remarkable agent; indigo, for example, which resists the action of strong oil of vitriol, is converted by chlorine into a brownish substance, to which the blue color cannot be restored. The presence of water is essential to these changes, for the gas in a state of perfect dryness is incapable even of affecting litmus.

Chlorine is largely used in the arts for bleaching linen and cotton goods, rags for the manufacture of paper, &c. For these purposes, it is sometimes employed in the state of gas, sometimes in that of solution in water, but more frequently in combination with lime, forming the substance called bleaching-powder. When required in large quantities, it is usually made by pouring slightly diluted oil of vitriol upon a mixture of common salt and oxide of manganese contained in a large leaden vessel. The decomposition which ensues may be thus represented:—



Chlorine is one of the best and most potent substances that can be used for the purpose of disinfection, but its employment requires care. Bleaching-powder mixed with water and exposed to the air in shallow vessels, becomes slowly decomposed by the carbonic acid of the atmosphere, and the chlorine evolved; if a more rapid disengagement be wished, a little acid of any kind may be added. In the absence of bleaching-powder, either of the methods for the production of the gas described may be had recourse to, always taking care to avoid an excess.

Chloride of hydrogen; hydrochloric, chlorohydric, or muriatic acid.—This substance, in a state of solution in water, has been long known. The gas is prepared with the utmost ease by heating in a flask, fitted with a cork and

bent tube, a mixture of common salt and oil of vitriol, diluted with a small quantity of water; it must be collected by displacement, or over mercury. It is a colorless gas, which fumes strongly in the air from condensing the atmospheric moisture; it has an acid, suffocating odor, but is infinitely less offensive than chlorine. Exposed to a pressure of 40 atmospheres, it liquefies.

Hydrochloric acid gas has a density of 1·269. It is exceedingly soluble in water, that liquid taking up at the temperature of the air about 418 times its bulk. The gas and solution are powerfully acid.

The action of oil of vitriol on common salt, or any analogous substance, is thus easily explained:—

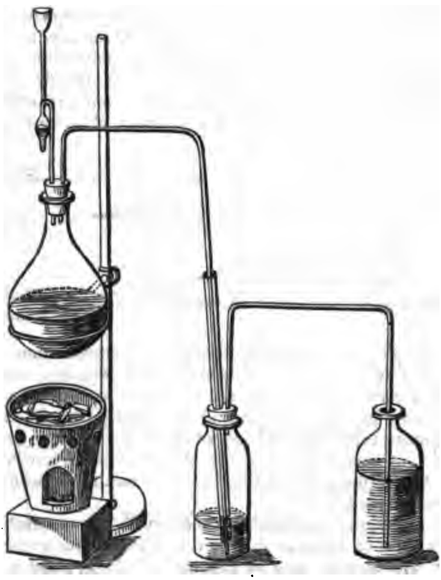
Chloride sodium	Chlorine Sodium	Hydrochloric acid.
Water . . .	Hydrogen Oxygen	
Sulphuric acid		Sulphate of soda.

The composition of this substance may be determined by synthesis; when a measure of chlorine and a measure of hydrogen are fired by the electric spark, two measures of hydrochloric acid gas result, the combination being unattended by change of volume. By weight, it contains 35·41 parts chlorine and 1 part hydrogen.

Solution of hydrochloric acid, the liquid acid of commerce, is a very important preparation, and of extensive use in chemical pursuits; it is best prepared by the following arrangement:—

A large glass flask, containing a quantity of common salt, is fitted with a

Fig. 99.



cork and bent tube, in the manner represented; the latter passes through and below a second short tube into a wide-necked bottle, containing a little water, into which the open tube dips. A bent tube, adapted to another hole in the cork of the wash-bottle, serves to convey the purified gas into a quantity of distilled water, by which it is instantly absorbed. The joints are made air-tight by melting over the corks a little yellow wax.

Oil of vitriol, about equal in weight to the salt, is then slowly introduced by the funnel; the disengaged gas is at first wholly absorbed by the water in the wash-bottle, but when this becomes saturated, it passes into the second vessel and there dissolves. When all the acid has been added, heat may be applied to the flask by a charcoal chauffer, until its contents appear nearly dry, and the evolution of gas almost ceases, when the process may be stopped. As much heat is given out during the condensation of the gas, it is necessary to surround the condensing-vessel with cold water.

The simple wash bottle figured in the drawing will be found an exceedingly useful contrivance in a great number of chemical operations. It serves in the present, and in many similar cases, to retain any liquid or solid matter mechanically carried over with the gas, and it may be always employed when gas of any kind is to be passed through an alkaline or other solution. The open tube dipping into the liquid prevents the possibility of absorption, by which a partial vacuum would be occasioned and the liquid of the second vessel lost by being driven into the first.

Fig. 100.

The arrangement by which the acid is introduced also deserves a moment's notice. The tube is bent twice upon itself, and a bulb blown in one portion. Liquid poured into the funnel rises upon the opposite side of the first bend until it reaches the second; it then flows over and runs into the flask. Any quantity can then be got into the latter without the introduction of air, and without the escape of gas from the interior. The funnel acts also as a kind of safety-valve, and in both directions, for if by any chance the delivery-tube should be stopped and the issue of gas prevented, its increased elastic force soon drives the little column of liquid out of the tube, the gas escapes, and the vessel is saved. On the other hand, any absorption within is quickly compensated by the entrance of air through the liquid in the bulb. The plan employed on the great scale by the manufacturer is the same in principle as that described; he merely substitutes a large iron cylinder for the flask, and vessels of stone-ware for those of the glass.

Pure solution of hydrochloric acid is transparent and colorless; when strong, it fumes in the air by disengaging a little gas. It leaves no residue on evaporation, and gives no precipitate or milkiness with solution of chloride of barium. When saturated with the gas, it has a specific gravity of 1·21, and contains about 42 per cent. of real acid. The commercial acid has usually a yellow color and is very impure, containing salts, sulphuric acid, chloride of iron, and organic matter. It may be rendered sufficiently good for most purposes by diluting it to the density of 1·1, which happens when the strong acid is mixed with its own bulk or rather less of water, and then distilling it in a retort furnished with a Liebig's condenser.

A mixture of nitric and hydrochloric acids has long been known under the name of *aqua regia*, from its property of dissolving gold. When these two substances are heated together, they both undergo decomposition, nitrous acid and chlorine being evolved; it is the chlorine which attacks the metal.

The presence of hydrochloric acid, or any other soluble chloride, is easily detected by solution of nitrate of silver. A white curdy precipitate is pro-

duced, insoluble in nitric acid, freely soluble in ammonia, and subject to blacken by exposure to light.

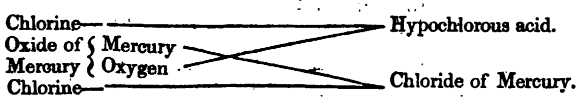
Compounds of Chlorine and Oxygen.

Although these bodies never combine directly, they may be made to unite by circuitous means in four different proportions, as below:—

	Composition by weight.	
	Chlorine.	Oxygen.
Hypochlorous acid	35·41	8
Chlorous acid	35·41	32
Chloric acid	35·41	40
Hyperchloric acid*	25·41	56

Hypochlorous acid.—Produced by the action of chlorine gas upon red oxide of mercury. It is a pale yellow gaseous body, containing in every two measures, two measures of chlorine and one of oxygen. It is very freely soluble in water, and explodes, although with no great violence, by slight elevation of temperature. The odor of this gas somewhat resembles that of chlorine. It bleaches powerfully, and acts upon certain of the metals in a manner which is determined by their respective attractions for oxygen and chlorine. It forms with the alkalies a series of bleaching salts.

The reaction by which hypochlorous acid is produced may thus be illustrated:—



The chloride of mercury, however, does not remain as such; it combines with another portion of the oxide, when the latter is in excess, forming a peculiar brown compound, an oxychloride of mercury.†

Chlorous acid; peroxide of chlorine.—Chlorate of potash is made into a paste with sulphuric acid, previously diluted with half its weight of water and cooled; this is introduced into a small glass retort, and very cautiously heated by warm water; a deep yellow gas is evolved, which is the body in question; it may be collected over mercury.

Peroxide of chlorine has a powerful odor, quite different from that of chlorine itself. It is exceedingly explosive, being resolved with violence into its elements by a temperature short of the boiling point of water. It is composed by measure of two volumes chlorine and four volumes oxygen, condensed into four volumes. It may be liquefied by pressure. Water dissolves this gas pretty freely, and the solution bleaches. It is said to form salts with the alkalies.

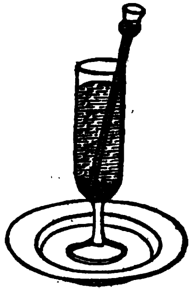
* Hypochlorous acid . . . . . $Cl\,O$
Chlorous acid . . . . $Cl\,O_4$
Chloric acid . . . . $Cl\,O_5$
Hyperchloric acid . . . . $Cl\,O_7$

† A very commodious method of preparing hypochlorous acid has lately been described by M. Pelouze. Red oxide of mercury, prepared by precipitation and dried by exposure to a strong heat, is introduced into a glass tube, kept cool, and well-washed, dry chlorine gas slowly passed over it. Chloride of mercury and hypochlorous acid are formed; the latter is collected by displacement. When the flask or bottle in which the gas is received is exposed to artificial cold by the aid of a mixture of ice and salt, the hypochlorous acid condenses to a deep red liquid, slowly soluble in water, and very subject to explosion. It is remarkable that the *crystalline* oxide of mercury prepared by calcining the nitrate, or by the direct oxidation of the metal, is scarcely acted upon by chlorine under the circumstances described.—Ann. Chim. et Phys., 3d. Series, vii. p. 179.

The production of chlorous acid from chlorate of potash and sulphuric acid depends upon the spontaneous splitting of the chloric acid into chlorous acid and hyperchloric acid, which latter remains in union with the potash.*

When a mixture of chlorate of potash and sugar is touched with a drop of oil of vitriol, it is instantly set on fire; the chlorous acid disengaged being decomposed by the combustible substance with such violence as to cause inflammation. If crystals of chlorate of potash be thrown into a glass of water, a few small fragments of phosphorus added, and then oil of vitriol poured down a narrow funnel reaching to the bottom of the glass, the phosphorus will burn beneath the surface of the water, by the assistance of the oxygen of the chlorous acid disengaged. The liquid at the same time becomes yellow, and acquires the odor of that gas.

Fig. 101.



Chloric acid.—This is the most important compound of the series. When chlorine is passed to saturation into a moderately strong solution of caustic potash, and the liquid concentrated by evaporation, it furnishes on cooling flat tabular crystals of a colorless salt, consisting of potash combined with chloric acid. The mother liquor contains chloride of potassium. In this reaction a part of the potash is decomposed; its oxygen combines with one portion of chlorine to form chloric acid, while the potassium is taken up by a second portion of the same substance.†

When solution of caustic baryta is substituted for the potash, a chlorate of that base may be by a similar change obtained, and from this the acid itself may be prepared by precipitating the baryta by the requisite quantity of sulphuric acid.

By cautious evaporation the acid may be so far concentrated as to assume a syrupy consistence; it is then very easily decomposed. It sometimes sets fire to paper, or other dry organic matter, in consequence of the facility with which it is de-oxidized by combustible bodies.

The chlorates are easily recognized; they give no precipitate when in solution with nitrate of baryta or silver; they evolve pure oxygen when heated, passing thereby into chlorides; and they afford, when treated with sulphuric acid, the characteristic explosive yellow gas already described. The dilute solution of the acid has no bleaching power.

Hyperchloric acid.—Professor Penny has shown that when powdered chlorate of potash is heated with nitric acid, a change of the same description as that which happens when sulphuric acid is used takes place, but with this important difference that the chlorine and oxygen, instead of being evolved in a dangerous state of combination, are emitted in a state of *mixture*. The result of the reaction is a mixture of nitrate of potash and hyperchlorate of potash, which may be readily separated by their difference of solubility.

By boiling the potash salt with a solution of hydrofluosilicic acid, which

* 3 equiv. Chloric acid........ { 2 eq chlorine, 8 eq. oxygen → 2 eq. chlorous acid.
{ 7 eq. oxygen, 1 eq. chlorine → 1 eq. hyperchloric acid.

† 6 eq. chlorine { 5 eq. chlorine, 1 eq. chlorine
6 eq. potash { 5 eq. potassium, 5 eq. oxygen, 1 eq. potash

5 eq. chlorine + 5 eq. potassium → 5 eq. chloride potassium.
1 eq. chlorine + 5 eq. oxygen + 1 eq. potash → 1 eq. chlorate of potash.

forms an almost insoluble salt with potash, and then heating the filtered solution with a little silica, the acid may be obtained tolerably pure. It may be concentrated by evaporation, and even distilled without change. The solution fumes slightly in the air, and has a specific gravity of 1·65. It is very greedy of moisture, and has no bleaching properties. The hyperchlorates much resemble the chlorates; they give off oxygen when heated to redness. The acid is the most stable of the compounds of chlorine and oxygen.

IODINE.

This remarkable substance which was first noticed in 1812 by M. Courtois, of Paris, is found in combination with sodium or potassium to a small extent in sea-water, and occasionally in much larger proportion in that of certain mineral springs. It seems to be in some way beneficial to many marine plants, as these latter have the power of abstracting it from the surrounding water, and accumulating it in their tissues. It is from this source that all the iodine of commerce is derived.

Kelp, or the half-vitrified ashes of sea-weeds, prepared by the inhabitants of the Western Islands, and the northern shores of Scotland and Ireland, is treated with water, and the solution filtered. The liquid is then concentrated by evaporation until it is reduced to a very small volume, the chloride of sodium, carbonate of soda, chloride of potassium and other salts, being removed as they successively crystallize. The dark brown mother-liquor left contains very nearly the whole of the iodide; this is mixed with sulphuric acid and peroxide of manganese, and gently heated in a leaden retort, when the iodine distils over and condenses in the receiver. The theory of the operation is exactly analogous to that of the preparation of chlorine; it requires in practice, however, careful management, otherwise the impurities present in the solution interfere with the general result.

The manganese is not really essential; the iodide of potassium or sodium, heated with an excess of sulphuric acid, evolves iodine. It is probable that this effect is due to a secondary action between the hydriodic acid first produced and the residue of the sulphuric acid in which both suffer decomposition, yielding iodine, water, and sulphurous acid.

Iodine crystallizes in plates or scales of a bluish-black color and imperfect metallic lustre, resembling that of plumbago; the crystals are sometimes very large and brilliant. Its density is 4·948. At 225° it fuses, and at 347° boils, the vapor having an exceedingly beautiful violet color.* It is slowly volatile, however, at common temperature, and exhales an odor much resembling that of chlorine. The density of the vapor is 8·716. Iodine requires for solution about 7000 parts of water, which nevertheless acquires a brown color; in alcohol it is much more freely soluble. Solutions of hydriodic acid and the iodides of the alkaline metals also dissolve a large quantity; these solutions are not decomposed by water, which is the case with the alcoholic tincture.

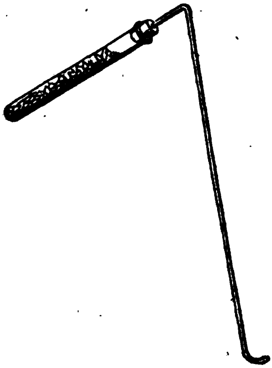
This substance stains the skin, but not permanently; it has a very energetic action upon the animal system, and is much used in medicine.

One of the most characteristic properties of iodine is the production of a splendid blue color by contact with the organic principle starch. The iodine for this purpose must be free or uncombined, and the solution of starch cold. It is easy, however, to make the test available for the purpose of recognizing the presence of the element in question when a soluble iodide is suspected; it is only necessary to add a very small quantity of chlorine-water, when the iodine being displaced from combination, becomes capable of acting upon the starch.

* Whence the name, from ἰώδης, violet-colored.

Hydriodic acid.—The simplest process for preparing hydriodic acid gas is to introduce into a glass tube, sealed at one extremity, a little iodine, then a small quantity of roughly powdered glass moistened with water, upon this a few little fragments of phosphorus, and lastly more glass; this order of iodine, glass, phosphorus, glass, is repeated until the tube is half or two-thirds filled. A cork and narrow bent tube are then fitted, and gentle heat applied. The gas is received over mercury. The experiment depends upon the formation of an iodide of phosphorus, and its subsequent decomposition by water, hydrated phosphorous acid and iodide of hydrogen being produced. The glass merely serves to moderate the violence of the action of the iodine upon the phosphorus.

Fig. 102



Hydriodic acid gas greatly resembles the corresponding chlorine compound; it is colorless, and highly acid; it fumes in the air, and is very soluble in water. Its density is about 4·4. By weight it is composed of 126·36 parts iodine and 1 part hydrogen, and by measure, of equal volumes of iodine, vapor and hydrogen united without condensation.*

Solution of hydriodic acid may be prepared by a process much less troublesome than the above. Iodine in fine powder is suspended in water, and a stream of washed sulphuretted hydrogen passed; sulphur is deposited, and the iodine converted into hydriodic acid. When the liquid has become colorless, it is heated to expel the excess of sulphuretted hydrogen, and filtered. This solution cannot long be kept, especially if it be strong; the oxygen of the air gradually decomposes the hydriodic acid, and iodine is set free, which, dissolving in the remainder, communicates to it a brown color.

Compounds of Iodine and Oxygen.

Two only are yet known; they are called iodic and hyperiodic acids.

	Composition by weight.	
	Iodine.	Oxygen.
Iodic acid	126·36	40
Hyperiodic acid†	126·36	56

Iodic acid may be prepared by the distinct oxidation of iodine by nitric acid of specific gravity 1·5; the materials are kept at a boiling temperature for several hours, or until the iodine has disappeared. The solution is then cautiously distilled to dryness, and the residue dissolved in water and made to crystallize.

Iodic acid is a very soluble substance; it crystallizes in colorless, six-sided tables, which contain water. It is decomposed by heat, and its solution readily de-oxidized by sulphurous acid. The iodates much resemble the chlorates; that of potash is decomposed by heat into iodide of potassium and oxygen gas.

Hyperiodic acid.—When solution of iodate of soda is mixed with caustic

* Hydriodic acid by intense cold and pressure has been both liquefied and solidified. Faraday, Lond. Atheneum, Feb. 1845.—R. B.

† IO_5, and IO_7.

soda, and a current of chlorine transmitted through the liquid, two salts are formed, namely, chloride of sodium and a combination of hyperiodate of soda with hydrate of soda, which is sparingly soluble. This is separated, converted into a silver-salt, and dissolved in nitric acid; the solution yields on evaporation crystals of yellow hyperiodide of silver; from which the acid may be separated by the action of water, which resolves the salt into free acid and insoluble sub-hyperiodate.

The acid itself may be obtained in crystals. It is permanent in the air, and capable of being resolved into iodine and oxygen by a high temperature.*

BROMINE.

Bromine† dates back to 1826 only, having been discovered by M. Balard of Montpellier. It is found in sea water, and is a frequent constituent of saline springs, chiefly as bromide of magnesium;—a celebrated spring of the kind exists near Kreutznach in Prussia. Bromine may be obtained pure by the following process, which depends upon the fact that ether agitated with an aqueous solution of bromine, removes the greater part of that substance.

The mother-liquor, from which the less soluble salts have been separated by crystallization, is exposed to a stream of chlorine, and then shaken up with a quantity of ether; the chlorine decomposes the bromide of magnesium, and the ether dissolves the bromine thus set free. On standing, the ethereal solution, having a fine red color, separates. Caustic potash is then added; bromide of potassium and bromate of potash are formed. The solution is evaporated to dryness, and the saline matter heated in a small retort with oxide of manganese and sulphuric acid diluted with a little water, the neck of the retort being plunged into cold water. The bromine volatilizes in the form of a deep red vapor, which condenses into drops beneath the liquid.

Bromine is at common temperatures a red thin liquid of an exceedingly intense color, and very volatile: it freezes at a little below 0°, and boils at 116°. The density of the liquid is 2·96, and that of the vapor 5·393. The odor of bromine is very suffocating and offensive, much resembling that of iodine, but more disagreeable. It is slightly soluble in water, more freely in alcohol, and most abundantly in ether. The aqueous solution bleaches.

Hydrobromic acid.—This substance bears the closest resemblance in every particular to hydriodic acid; it has the same constitution by volume, very nearly the same properties, and may be prepared by means exactly similar, substituting the one body for the other. The solution of hydrobromic acid has also the power of dissolving a large quantity of bromine, thereby acquiring a red tint. Hydrobromic acid contains by weight 78·26 parts bromine, and 1 part hydrogen.

Bromic acid.—Caustic alkalies in presence of bromine undergo the same change as with chlorine, bromide of the metal, and bromate of the oxide being produced; these may often be separated by the inferior solubility of the latter. Bromic acid, obtained from bromate of baryta, closely resembles chloric acid; it is easily decomposed. The bromates when heated lose oxygen and become bromides.

No other compound of bromine and oxygen has yet been described.

FLUORINE.

This element has never been isolated; its properties are consequently unknown. The compounds containing fluorine can be easily decomposed, and the element transferred from one body to another; but its extraordinary che-

* Graham, Elements, p. 281.

† From βρῶμος, a noisome smell: a very appropriate term.

mical energies towards the metals and towards silicon, a component of glass have hitherto baffled all attempts to obtain it in a separate state.*

Hydrofluoric acid.—When powdered fluoride of calcium (fluor-spar) is heated with concentrated sulphuric acid in a retort of platinum connected with a carefully cooled receiver of the same metal, a very volatile colorless liquid is obtained, which emits copious white and highly suffocating fumes in the air. This is the acid in an anhydrous state.

When hydrofluoric acid is put into water, it unites with the latter with great violence; the dilute solution attacks glass with great facility. The concentrated acid dropped upon the skin is said to occasion deep and malignant ulcers, so that great care is requisite in its management. Hydrofluoric acid contains 18·78 parts fluorine and 1 part hydrogen.

In a diluted state, this acid is occasionally used in the analyses of siliceous minerals, when alkali is to be estimated; it is employed also for etching on glass, for which purpose the acid may be prepared in vessels of lead, that metal being but slowly attacked under these circumstances. The vapor of the acid is also very advantageously applied to the same object in the following manner; the glass to be engraved is coated with etching-ground or wax, and the design traced in the usual way with a pointed instrument. A shallow basin made by beating up a piece of sheet lead is then prepared, a little powdered fluor-spar placed in it, and enough sulphuric acid added to form with the latter a thin paste. The glass is placed upon the basin, with the waxed side downwards, and gentle heat applied beneath, which speedily disengages the vapor of hydrofluoric acid. In a very few minutes the operation is complete; the glass is then removed and cleaned by a little warm oil of turpentine. When the experiment is successful, the lines are very clear and smooth.

No combination of fluorine and oxygen has yet been discovered.

SILICON.

Silicon, sometimes called silicium, in union with oxygen, constituting silica or the earth of flints, is a very abundant substance, and one of great importance. It enters largely into the composition of many of the rocks and mineral masses of which the surface of the earth is composed. The following process yields silicon most readily. The double fluoride of silicon and potassium is heated in a glass tube, with nearly its own weight of metallic potassium; violent reaction ensues, and silicon is set free. When cold, the contents of the tube are put into cold water, which removes the saline matter and any residual potassium, and leaves untouched the silicon. So prepared, silicon is a dark brown powder, destitute of lustre. Heated in the air it burns, and becomes superficially converted into silica. It is also acted upon by sulphur and by chlorine. When silicon is strongly heated in a covered crucible, its properties are greatly changed: it becomes darker in color, denser, and incombustible, refusing to burn even when heated by the flame of the oxyhydrogen blow-pipe.

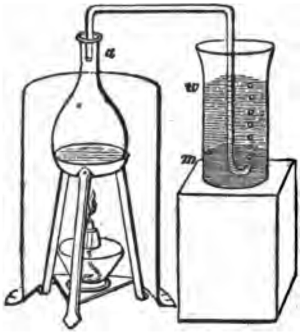
Silica. Silicic acid.—This is the only known oxide; it contains 22·18 parts silicon, and 24 parts oxygen.† Colorless transparent rock crystal consists of silica very nearly in a state of purity; common quartz, agate, calcedony, flint, and several other minerals, are also chiefly composed of this substance.

* Fluorine has been procured in a free state by M. Baudrimont, by a method similar to that for chlorine. It is a gas of a brownish red color, odor that of chlorine and burnt sugar. It has bleaching powers; does not act on glass; sp. gr. 1·3. Combines directly with gold. (Ed. Phil. Mag., vol. x. p. 149.)—R. B.

† Or, $Si\,O_2$.

The experiment about to be described furnishes silica in a state of complete purity, and at the same time exhibits one of the most remarkable properties of silicon, namely, its attraction for fluorine. A mixture is made of equal parts fluor-spar and glass, both finely powdered, and introduced into a glass flask, *a*, with a quantity of oil of vitriol. A tolerably wide bent tube, fitted to the flask by a cork, passes to the bottom of a glass jar, into which enough mercury is poured to cover the extremity of the tube, *m*. The jar is then half filled with water, *w*, and heat is applied to the flask.

Fig. 103.



The first effect is the disengagement of hydrofluoric acid; this substance, however, finding itself in contact with the silica of the powdered glass, undergoes decomposition, water and fluoride of silicon being produced. The latter is a permanent gas, which escapes from the flask by the bent tube. By contact with a large quantity of water, it is in turn decomposed, yielding silica, which separates in a beautiful gelatinous condition, and an acid liquid which is a double fluoride of silicon and hydrogen, commonly called hydrofluosilicic acid.* The silica may be collected on a cloth filter, well washed, dried, and heated to redness, to expel water.

The acid liquid is kept as a test for potash, with which it forms a nearly insoluble precipitate, the double fluoride of silicon and potassium, used in the preparation of silicon. The fluoride of silicon, instead of being conducted into water, may be collected over mercury; it is a permanent gas, destitute of color and very heavy. Admitted into the air, it condenses the moisture of the latter, giving rise to a thick white cloud. It is important in the experiment above described to keep the end of the delivery-tube from touching the water of the jar, otherwise it almost instantly becomes stopped; the mercury effects this object.

There is another method by which pure silica can be prepared, and which is also very instructive, inasmuch as it is the basis of the proceeding adopted in the analysis of all siliceous minerals. Powdered rock-crystal or fine sand is mixed with about three times its weight of dry carbonate of soda, and the mixture fused in a platinum crucible. When cold, the glassy mass is boiled with water, by which it is softened, and in great part dissolved. An excess of hydrochloric acid is then added, and the whole evaporated to complete dryness. By this treatment the gelatinous silica thrown down by the acid becomes completely insoluble, and remains behind when the dry saline mass is treated with acidulated water, by which the alkaline salts, alumina, oxide

* (1) Reaction of hydrofluoric acid upon silica:—

Hydrofluoric acid . { Fluorine, Hydrogen } ——— Gaseous fluoride of silicon.
Silica . { Silicon, Oxygen } ——— Water.

(2) Decomposition of fluoride of silicon by water:—

Fluoride of silicon { Silicon, Fluorine } ——— Silica.
Water { Oxygen, Hydrogen }
Fluoride of Silicon ——— Hydrofluosilicic acid.

of iron, lime, and many other bodies which may happen to be present, are removed. The silica is washed, dried, and heated red-hot.

The most prominent characters of silica are the following: it is a very fine, white, tasteless powder, not sensibly soluble in water or dilute acids (with the exception of hydrofluoric) unless recently precipitated. It dissolves, on the contrary, freely in strong alkaline solutions. Its density is about 2·66, and it is only to be fused by the oxyhydrogen blow-pipe.

Silica is in reality an acid, and a very powerful one; insolubility in water prevents the manifestation of acid properties under ordinary circumstances. When heated with bases, especially those which are capable of undergoing fusion, it unites with them and forms true salts, which are sometimes soluble in water, as in the case of the silicates of potash and soda when the proportion of base is considerable. Common glass is a mixture of several silicates in which the reverse of this happens, the silica, or, as it is more correctly called, silicic acid, being in excess. Even glass, however, is slowly acted upon by water.

Finely divided silica is highly useful in the manufacture of porcelain.

BORON.

This substance is closely related to silicon; it is the basis of boracic acid.

Boron is prepared by a process very similar to that described in the case of silicon, the double fluoride of boron and potassium being substituted for the other salt, and the operation conducted in a small iron vessel, instead of a glass tube. It is a dull greenish brown powder, which burns in the air when heated, producing boracic acid. Nitric acid, alkalies in a fused condition, chlorine, and other agents, attack it readily.

There is but one oxide of boron, namely *boracic acid*, containing 10·9 parts boron, and 24 parts oxygen.*

Boracic acid is found in solution in the water of the hot volcanic lagoons of Tuscany, whence a large supply is at present derived. It is also easily made by decomposing with sulphuric acid a hot solution of borax, a salt brought from the East Indies, consisting of boracic acid combined with soda.

Boracic acid crystalizes in transparent colorless plates, soluble in about 25 parts of cold water, and in a much smaller quantity at a boiling heat; the acid has but little taste, and feebly affects vegetable colors. When heated, it loses water, and melts to a glassy transparent mass, which dissolves many metallic oxides with great ease. The crystals contain 34·9 parts real acid, and 27 parts water. They dissolve in alcohol, and the solution burns with a green flame.

Glassy boracic acid in a state of fusion, is quite fixed in the fire; the solution in water cannot, however, be evaporated without very appreciable loss by volatilization; hence it is probable that the hydrate is far more volatile than the acid itself.

By heating in a glass flask or retort one part of the vitrified boracic acid, 2 of fluor-spar, and 12 of oil of vitriol, a gaseous fluoride of boron may be obtained, and received in glass jars standing over mercury. It is a transparent gas, very soluble in water, and very heavy; it forms a dense fume in the air like the fluoride of silicon.†

* BO_3.

† These two bodies are thus constituted:—SiF_3 and BF_3.

ON CERTAIN IMPORTANT COMPOUNDS FORMED BY THE UNION OF THE PRECEDING ELEMENTS AMONG THEMSELVES.

COMPOUNDS OF CARBON AND HYDROGEN.

THE compounds of carbon and hydrogen already known are exceedingly numerous; perhaps all, in strictness, belong to the domain of organic chemistry, as they cannot be formed by the direct union of their elements, but always arise from the decomposition of a complex body of organic origin. It will be found convenient, notwithstanding, to describe two of them in this part of the volume, as they very well illustrate the important subjects of combustion, and the nature of flame.

Light carburetted hydrogen; marsh-gas; fire-damp; gas of the acetates.—This gas is but too often found to be abundantly disengaged in coal-mines from the fresh cut surface of the coal, and from remarkable apertures or "blowers," which emit for a great length of time a copious stream or jet of gas, which probably existed in a state of compression, pent up in the coal.

The mud at the bottom of pools in which water-plants grow, on being stirred, suffers bubbles of gas to escape, which may be easily collected. This, on examination, is found to be chiefly a mixture of light carburetted hydrogen and carbonic acid; the latter is easily absorbed by lime-water or caustic potash.

Until quite recently, no method was known by which the gas in question could be produced in a state approaching to purity by artificial means; the various illuminating gases from pit-coal and oil, and that obtained by passing the vapor of alcohol through a red-hot tube, contain large quantities of light carburetted hydrogen, associated, however, with other substances which hardly admit of separation. M. Dumas has at length discovered a method by which that gas can be produced at will, perfectly pure, and in any quantity.

A mixture is made of 4 parts crystallized acetate of soda, 4 parts solid hydrate of potash, and 6 parts quicklime in powder. This mixture is transferred to a flask or retort, and strongly heated; the gas is disengaged in great abundance, and may be received over water.*

Light carburetted hydrogen is a colorless and nearly inodorous gas, which does not affect vegetable colors. It burns with a yellow flame, generating carbonic acid and water. It is not poisonous, and may be respired to a great extent without apparent injury. The density of this compound is about ·559, 100 cubic inches weighing 17·41 grains; and it contains carbon and hydrogen associated in the proportion of 6 parts by weight of the former to 2 of the latter.†

* Ann. Chim. et Phys., lxxiii. p. 93. The reaction consists in the conversion of the acetic acid, by the aid of the elements of water, into carbonic acid and light carburetted hydrogen; the instability of the organic acid at a high temperature, and the attraction of the potash for carbonic acid, being the determining causes. The lime prevents the hydrate of potash from fusing and attacking the glass vessels. All these decompositions are best understood by putting them in the shape of an equation.

$$\left.\begin{array}{ll}\text{Acetic acid} & C_4H_3O_3\\ \text{Water} & \underline{\quad HO\quad}\\ & C_4H_4O_4\end{array}\right\} = \left\{\begin{array}{ll}\text{Carbonic acid, 2 eq.} & C_2\quad O_4\\ \text{Marsh gas, 2 eq.} & \underline{C_2H_4\quad}\\ & C_4H_4O_4\end{array}\right.$$

† The two carburets of hydrogen here described are thus represented in equivalents:—

Light carburetted hydrogen	$C\ H_2$
Olefiant gas	$C_2\ H_2$

When 100 measures of this gas are mixed with 200 of pure oxygen in the endiometer, and the mixture exploded by the electric spark, 100 measures of a gas remain, which is entirely absorbable by a little solution of caustic potash. Now carbonic acid contains its own volume of oxygen; one-half the oxygen added, that is, 100 measures, must have been consumed in uniting with the hydrogen. Consequently, the gas must contain twice its own measure of hydrogen, and enough carbon to produce, when completely burned, an equal quantity of carbonic acid.

When chlorine is mixed with light carburetted hydrogen over water, no change follows, provided light be excluded. The presence of light, however, brings about decomposition, hydrochloric acid, carbonic acid, and sometimes carbonic oxide being produced. It is important to remember that the gas is not acted upon by chlorine in the dark.

Olefiant gas.—Strong spirit of wine is mixed with five or six times its weight of oil of vitriol in a glass-flask, the tube of which passes into a wash-bottle containing caustic potash. A second wash-bottle, partly filled with oil of vitriol, is connected to the first, and furnished with a tube dipping into the water of the pneumatic trough. On the first application of heat to the contents of the flask, alcohol, and afterwards ether, make their appearance; but as the temperature rises, and the mixture blackens, the ether-vapor diminishes in quantity, and its place becomes in great part supplied by a permanent inflammable gas; carbonic acid and sulphurous acid are also generated at the same time, besides traces of other products. The two last-mentioned gases are absorbed by the alkali in the first bottle, and the ether-vapor by the acid in the second, so that the olefiant gas is delivered tolerably pure. The reaction is too complex to be discussed at the present moment; it will be found fully described in another part of the volume. Olefiant gas thus produced is colorless, neutral, and but slightly soluble in water. It has a faint odor of garlic. On the approach of a kindled taper it takes fire, and burns with a splendid white light, far surpassing in brilliancy that produced by light carburetted hydrogen. This gas, when mixed with oxygen and fired, explodes with great violence. Its density is ·981; 100 cubic inches weigh 30·57 grains.*

By the use of the eudiometer, as already described, it has been found that each measure of olefiant gas requires for complete combustion exactly three of oxygen, and produces under these circumstances two measures of carbonic acid. Whence it is evident that it contains twice its own volume of hydrogen, combined with twice as much carbon as in marsh-gas.

By weight, these proportions will be 12 parts carbon, and 2 parts hydrogen.

Olefiant gas is decomposed by passing through a tube heated to bright redness; a deposit of charcoal takes place, and the gas becomes converted into light carburetted hydrogen, or even into free hydrogen, if the temperature be very high. This latter change is of course attended by increase of volume.

Chlorine acts upon olefiant gas in a very remarkable manner. When the two bodies are mixed, even in the dark, they combine in equal measures, and give rise to a heavy oily liquid, of sweetish taste and ethereal odor, to which the name chloride of hydrocarbon, or Dutch liquid, is given. It is from this peculiarity that the term *olefiant* is derived.

A pleasing and instructive experiment may also be made by mixing in a tall jar two measures of chlorine and one of olefiant gas, and then quickly applying a light to the mouth of the vessel. The chlorine and hydrogen unite

* Olefiant gas by pressure and intense cold produced by the evaporation in a vacuum of solid carbonic acid and ether, is condensed into a colorless transparent liquid, but not frozen. Faraday.—R. B.

with flame, which passes quickly down the jar, while the whole of the carbon is set free in the form of a thick black smoke.

Coal and oil-gases.—The manufacture of coal gas is at the present moment a branch of industry of great interest and importance in several points of view. The process is one of great simplicity of principle, but requires, in practice, some delicacy of management to yield a good result.

When pit-coal is subjected to destructive distillation, a variety of products show themselves; permanent gases, steam, and vapors of tar, and volatile oils, besides a not inconsiderable quantity of ammonia from the nitrogen, always present in the coal. These substances vary very much in their proportions with the temperature at which the process is conducted, the permanent gases becoming more abundant with increased heat, but at the same time losing much of their value for the purposes of illumination.

The coal is distilled in cast-iron retorts, maintained at a bright red heat, and the volatilized products conducted into a long horizontal pipe of large dimensions, always half filled with liquid, into which dips the extremity of each separate tube; this is called the hydraulic main. The gas and its accompanying vapors are next made to traverse a refrigerator, usually a series of iron pipes, cooled on the outside by a stream of water; here the condensation of the tar and ammoniacal liquid becomes complete, and the gas proceeds onwards to another part of the apparatus, in which it is to be deprived of the sulphuretted hydrogen and carbonic acid gases always present in the crude product. This is effected by hydrate of lime, which readily absorbs the compounds in question. The purifiers are large iron vessels, partly filled with a mixture of hydrate of lime and water, in which a churning machine or agitator is kept in constant motion to prevent the subsidence of the lime. The gas is admitted at the bottom of the vessel, by a great number of minute apertures, and is thus made to present a large surface of contact to the purifying liquid. The last part of the operation, which indeed is often omitted, consists in passing the gas through dilute sulphuric acid, in order to remove a little ammonia which yet lingers behind. The quantity thus separated is very small; but in an extensive work even this little is worth preserving.

Coal-gas, thus manufactured and purified, is preserved for use in immense cylindrical receivers, close at the top, suspended in tanks of water by chains to which counterpoises are attached, so that the gas-holders rise and sink in the liquid as they become filled from the purifiers, or emptied by the mains. These latter are made of large diameter, to diminish as much as possible the resistance experienced by the gas in passing through such a length of pipe. The joints of these mains are yet made in such an imperfect manner, that immense loss is experienced by leakage when the pressure upon the gas at the works exceeds that exerted by a column of water an inch in height.*

Coal gas varies very much in composition, judging from its variable density and illuminating power, and from the imperfect analyses which have been made. The difficulties of such investigations are very great, and the results merely approximative. The purified gas is believed to contain the following substances, of which the first is most abundant, and the second most valuable.

* It may give some idea of the extent of this species of manufacture to mention, that in the year 1838 for lighting London and the suburbs alone, there were eighteen public gas works, and £2,800,000, invested in pipes and apparatus. The yearly revenue amounted to £450,000 and the consumption of coal in the same period to 180,000 tons, 1460 *millions* of cubic feet of gas being made in the year. There were 134,300 private lights, and 30,400 street-lamps. 890 tons of coal were used in the retorts in the space of twenty-four hours at mid-winter, and 7,120,000 cubic feet of gas consumed in the longest night.—Dr. Ure, Dictionary of Arts and Manufactures.

Light carburetted hydrogen.
Olefiant gas.
Hydrogen.
Carbonic oxide.
Nitrogen.
Vapors of volatile liquid carburets of hydrogen.*
Vapor of bisulphuret of carbon.

Separated by Condensation and by the Purifiers.

Tar and volatile oils.
Sulphate of ammonia, chloride and sulphuret of ammonium.
Sulphuretted hydrogen.
Carbonic acid.
Hydrocyanic acid, or cyanide of ammonium.

A very far better illuminating gas may be prepared from oil, by dropping it into a red-hot iron retort filled with coke; the liquid is in great part decomposed and converted into permanent gas, which requires no purification, as it is quite free from the ammoniacal and sulphur compounds, which vitiate the gas from coal. A few years ago this article was prepared in London; it was compressed for the use of the consumer into strong iron vessels, to the extent of 30 atmospheres; these were furnished with a screw-valve of peculiar construction, and exchanged for others when exhausted. The comparative high price of the material, and other circumstances, led to the abandonment of the undertaking.

COMBUSTION, AND THE STRUCTURE OF FLAME.

When any solid substance, capable of bearing the fire, is heated to a certain point, it emits light, the character of which depends upon the temperature. Thus, a bar of platinum or a piece of porcelain raised to a particular temperature, becomes what is called red-hot or emissive of red light; at a higher degree of heat this light becomes whiter and more intense, and when urged to the utmost, as in the case of a piece of lime placed in the flame of the oxyhydrogen blow-pipe, the light becomes exceedingly powerful, and acquires a tint of violet. Bodies in these states are said to be *incandescent* or *ignited.*

Again, if the same experiment be made on a piece of charcoal, similar effects will be observed, but something in addition; for whereas the platinum or porcelain, when removed from the fire, or the lime from the blow-pipe flame, begin immediately to cool, and emit less and less light, until they become completely obscure, the charcoal maintains to a great extent its high temperature. Unlike the other bodies too, which suffer no change whatever either of weight or substance, the charcoal gradually wastes away until it disappears. This is what is called *combustion*, in contradistinction to mere ignition; the charcoal burns, and its temperature is kept up by the heat evolved in the act of union with the oxygen of the air.

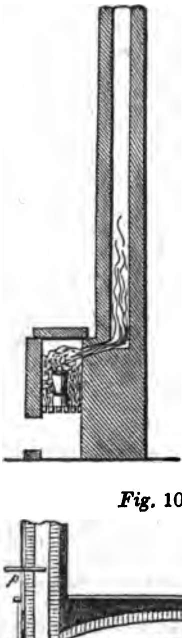
In the most general sense, a body in a state of combustion is one in the act of undergoing intense chemical action; any chemical action whatsoever, if its energy rise sufficiently high, may produce the phenomenon of combustion, by *heating the body to such an extent that it becomes luminous.*

In all ordinary cases of combustion, the action lies between the burning body and the oxygen of the air; and since the materials employed for the economi-

* These bodies increase the illuminating power, and confer on the gas its peculiar odor.

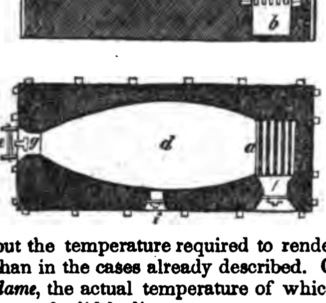
cal production of heat and light consist of carbon chiefly, or that substance conjoined with a certain proportion of hydrogen and oxygen, all common effects of this nature are cases of the rapid and violent oxidation of carbon and hydro gen by the aid of the free oxygen of the air. The heat must be referred to the act of chemical union, and the light to the elevated temperature.

Fig. 104.



By this principle it is easy to understand the means which must be adopted to increase the heat of ordinary fires to the point necessary to melt refractory metals, and to bring about certain desired effects of chemical decomposition. If the rate of consumption of the fuel can be increased by a more rapid introduction of air into the burning mass, the intensity of the heat will of necessity rise in the same ratio, there being reason to believe that the quantity of heat evolved is fixed and definite for the same constant quantity of chemical action. This increased supply of air may be effected by two distinct methods; it may be forced into the fire by bellows or blowing machines, as in the common forge, and in the blast and cupola-furnaces of the iron-worker, or it may be drawn through the burning materials by the help of a tall chimney, the fire-place being close on all sides, and no entrance of air allowed, save between the bars of the grate. Such is the kind of furnace generally employed by the scientific chemist in assaying and in the reduction of metallic oxides by charcoal; the principle will be at once understood by the aid of the sectional drawing, in which a crucible is represented arranged in the fire for an operation of the kind mentioned.

Fig. 105.



The "reverberatory" furnace is one very much used in the arts when substances are to be exposed to heat without contact with the fuel. The fire-chamber, *a*, is separated from the bed or hearth, *d d*, of the furnace by a low wall or *bridge*, *c*, of brick-work, and the flame and heated air are reflected downwards by the arched form of the roof. Any degree of heat can be obtained in a furnace of this kind, from the temperature of dull redness, to that required to melt very large quantities of cast-iron. The fire is urged by a chimney, provided with a sliding plate or damper, *p*, to regulate the draught.

Solids and liquids, as melted metal, enjoy, when sufficiently heated, the faculty of emitting light; the same power is possessed by gaseous bodies, but the temperature required to render a gas luminous is incomparably higher than in the cases already described. Gas or vapor in this condition constitutes *flame*, the actual temperature of which always far exceeds that of the white heat of solid bodies.

The light emitted from pure flame is exceedingly feeble; illuminating power is almost entirely dependent upon the presence of solid matter. The flame of hydrogen, or of the mixed gases, is scarcely visible in full day-light; in a dusty atmosphere, however, it becomes much more luminous by igniting to intense whiteness the floating particles with which it comes in contact. The piece of lime in the blow-pipe flame cannot have a higher temperature than that of the flame itself; yet the light it throws off is almost infinitely greater.

Flames burning in the air, and not supplied with oxygen from another source, are, as already stated, hollow; the chemical action is necessarily confined to the spot where the two bodies unite. That of a lamp or candle, when carefully examined, is seen to consist of three separate portions. The dark central part, A, easily rendered evident by depressing upon the flame a piece of fine wire gauze, consists of combustible matter drawn up by the capillarity of the wick, and volatilized by the heat. This is surrounded by a highly luminous cone or envelop, B, which, on contact with a cold body, deposits soot. On the outside a second cone, C, is to be traced, feeble in its light-giving power, but having an exceedingly high temperature. The explanation of these appearances is easy: carbon and hydrogen are very unequal in their attraction for oxygen, the latter greatly exceeding the former in this respect; consequently, when both are present, and the supply of oxygen limited, the hydrogen takes all, to the exclusion of a great part of the carbon. Now this happens in the case under consideration at some little distance within the outer surface of the flame, namely, in the luminous portion: the little oxygen which has penetrated thus far inwards is entirely consumed by the hydrogen, and the particles of deposited charcoal, which would, were they cooler, form smoke, become intensely ignited by the burning hydrogen, and evolve a light whose whiteness marks a very elevated temperature. In the exterior and scarcely visible cone, these particles of carbon undergo combustion.

Fig. 106.

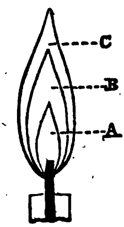
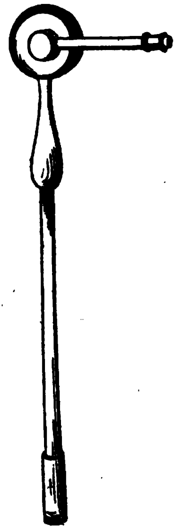


Fig. 107.

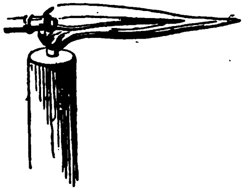


A jet of coal-gas exhibits these phenomena; but if the gas be previously mingled with air, or if air be forcibly mixed with, or driven into the flame, no such separation of carbon occurs, the hydrogen and carbon burn *together*, and the illuminating power almost disappears.

The common mouth blow-pipe is a little instrument of high utility; it is merely a brass tube, fitted with an ivory mouth-piece, and terminated by a jet, having a small aperture by which a current of air is driven across the flame of a candle. The best form is perhaps that contrived by Mr. Pepys, and figured in the margin. The flame so produced is very peculiar.

Instead of the double envelop just described, two long pointed cones are observed, which, when the blow-pipe is good, and the aperture, smooth and round, are very well defined, the outer cone being yellowish, and the inner blue. A double combustion is, in fact, going on, by the blast in the inside, and by the external air. The space between the inner and outer cones is filled with exceedingly hot combustible matter, possessing strong reducing or de-oxidizing powers, while the highly heated

Fig. 108.



air just beyond the point of the exterior cone oxidizes with great facility. A small portion of matter, supported on a piece of charcoal, or fixed in a ring at the end of a fine platinum wire, can thus in an instant be exposed to a very high degree of heat under these contrasted circumstances, and observations of great value made in a very short time. The use of the instrument requires an even and uninterrupted blast, of some duration, by a method easily acquired with a little patience; it consists in employing for the purpose the muscles of the cheeks alone, respiration being conducted through the nostrils, and the mouth from time to time replenished with air without intermission of the blast.

The Argand lamp, adapted to burn either oil or spirit, but especially the latter, is a very useful piece of chemical apparatus. In this lamp the wick is cylindrical, the flame being supplied with air both inside and outside; the combustion is greatly aided by the chimney, which is made of copper

Fig. 109.

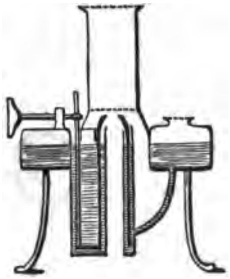
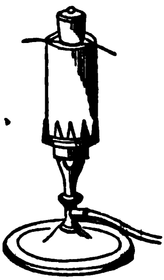


Fig. 110.

when the lamp is used as a source of heat. The accompanying drawing exhibits, in section, an excellent lamp of this kind for burning alcohol or wood-spirit. It is constructed of copper, and furnished with ground caps to the wick-holder and aperture* by which the spirit is introduced, in order to prevent loss when the lamp is not in use. Glass spirit lamps, fitted with caps to prevent evaporation, are very convenient for occasional use, being always ready and in order.

Fig. 111.



In London, and other large towns where coal-gas is to be had, that substance is constantly used with the greatest economy and advantage in every respect as a source of heat. Retorts, flasks, capsules, and other vessels, can be thus exposed to an easily regulated and invariable temperature for many successive hours. Small platinum crucibles may be ignited to redness by placing them over the flame on a little wire triangle. The arrangement shown, consisting of a common Argand gas burner fixed on a heavy and low foot and connected

* When in use this aperture must always be open, otherwise an accident is sure to happen; the heat expands the air in the lamp, and the spirit is forced out in a state of inflammation.

with a flexible tube of caoutchouc or other material, leaves nothing to desire.

The kindling-point, or temperature at which combustion commences, is very different with different substances; phosphorus will sometimes take fire in the hand; sulphur requires a temperature exceeding that of boiling water; charcoal must be heated to redness. Among gaseous bodies the same fact is observed: hydrogen is inflamed by a red-hot wire; carburetted hydrogen requires a white heat to effect the same thing. When flame is cooled by any means below the temperature at which the rapid oxidation of the combustible gas occurs, it is at once extinguished. Upon this depends the principle of Sir H. Davy's invaluable safe-lamp.

Mention has already been made of the frequent disengagement of great quantities of light carburetted hydrogen gas in coal-mines. This gas, mixed with seven or eight times its volume of atmospheric air, becomes highly explosive, taking fire at a light, and burning with a pale blue flame; and many fearful accidents have occurred from the ignition of large quantities of mixed gas and air occupying the extensive galleries and workings of a mine. Sir H. Davy undertook an investigation, with a view to discover some remedy for this constantly occurring calamity; his labors resulted in some exceedingly important discoveries respecting flame, of which the substance has been given, and which led to the construction of the lamp which bears his name.

When two vessels filled with a gaseous explosive mixture are connected by a narrow tube, and the contents of one fired by the electric spark or otherwise, the flame is not communicated to the other, provided the diameter of the tube, its length, and the conducting power for heat of its material, bear a certain proportion to each other; the flame is extinguished by cooling, and its transmission rendered impossible.

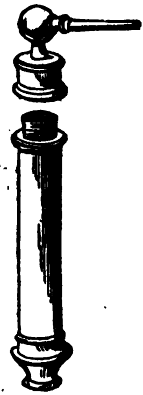
Fig. 112.

In this experiment high conducting power and diminished diameter compensate diminution of length; and to such an extent can this be carried, that metallic gauze, which may be looked upon as a series of very short square tubes arranged side by side, arrests in the most complete manner the passage of flame in explosive mixtures when of sufficient degree of fineness, depending upon the inflammability of the gas. Most providentially, the fire-damp mixture has an exceedingly high kindling point; a red-heat does not cause inflammation; consequently, a gauze will be safe for this substance, when flame would pass in almost any other case.

The miner's safe-lamp is merely an ordinary oil lamp, the flame of which is enclosed in a cage of wire-gauze, made double at the upper part, containing about 400 apertures to the square inch. The tube for supplying oil to the reservoir reaches nearly to the bottom of the latter, while the wick admits of being trimmed by a bent wire passing with friction through a small tube in the body of the lamp; the flame can thus be kept burning for any length of time, without the necessity of unscrewing the cage. When this lamp is taken into an explosive atmosphere, although the fire-damp may burn within the cage with such energy as sometimes to heat the metallic tissue to dull redness, the flame is never communicated to the mixture on the outside.

These effects may be conveniently studied by suspending the lamp in a

Fig. 113.



large glass jar, and gradually admitting coal-gas below. The oil-flame is at first elongated, and then as the proportion of gas increases, extinguished, while the interior of the gauze cylinder becomes filled with the burning mixture of gas and air. As the atmosphere becomes purer, the wick is once more relighted. These appearances are so remarkable, that the lamp becomes an admirable indicator of the state of the air in different parts of the mine.

The same great principle has been ingeniously applied by Mr. Hemming to the construction of the oxyhydrogen safety-jet formerly mentioned. This is a tube of brass about four inches long, filled with straight pieces of fine brass wire, the whole being tightly wedged together by a pointed rod, forcibly driven into the centre of the bundle. The arrangement thus presents a series of metal tubes, very long in proportion to their diameter, the cooling powers of which are so great as to prevent the possibility of the passage of flame, even with oxygen and hydrogen. The jet may be used, as before-mentioned, with a common bladder without a chance of explosion. The fundamental fact of flame being extinguished by contact with a cold body may be elegantly shown by twisting a copper wire into a short spiral, about ·1 inch in diameter, and then passing it *cold* over the flame of a wax candle; the latter is extinguished. Let the spiral be now heated to redness by a spirit lamp, and the experiment repeated; no such effect follows.*

Fig. 114.

NITROGEN AND HYDROGEN; AMMONIA.

When powdered sal-ammoniac is mixed with moist hydrate of lime, and gently heated in a gas-flask, a large quantity of gaseous matter is disengaged, which must be collected over mercury, or by displacement, advantage being taken of its low specific gravity.

Ammoniacal gas thus obtained is colorless; it has a very powerful pungent odor, and a strong alkaline reaction to test-paper, by which it may be at once distinguished from all other bodies possessing the same physical characters. Under a pressure of 6·5 atmospheres at 60°, ammonia condenses to the liquid form.† Water dissolves about 700 times its volume of this remarkable gas, forming a solution which in a more dilute state has long been known under the name of *liquor ammoniæ;* by heat, a great part is again expelled. The solution is decomposed by chlorine, sal-ammoniac being formed, and nitrogen set free.

* Where coal gas is to be had, it may be advantageously used as a source of heat, by taking advantage of the above-mentioned fact. On passing a current of gas through a wide vertical tube, open at the bottom to afford a free mixture with atmospheric air, but closed at the top by wire gauze, and then kindling the mixture after its escape through the meshes, it will burn with feeble illuminating power, but no loss of heat. When the proportion of the gas to the atmospheric air, is such as not to allow the flame to become yellow, the combustion will be complete, and no carbonaceous deposit will be formed on cold bodies held over the flames. The length and diameter of the cylinder are determined by the amount of gas to be burnt, and the length may be much decreased by interposing a second diaphragm of wire gauze about mid-length of the cylinder, the current of gas being introduced below this, by which means a more thorough and rapid mixture is made with the atmospheric air.—Sir John Robinson, K. H., &c., Ed. New Phil. Journal, 1840.—R. B.

† At the temperature of 103° F., liquid ammonia freezes into a colorless solid, heavier than the liquid itself.—Faraday.—R. B.

Ammonia has a density of ·589; 100 cubic inches weigh 18·26 grains. It cannot be formed by the direct union of its elements, although it is sometimes produced under rather remarkable circumstances by the de-oxidation of nitric acid. The great sources of ammonia are the feebly-compounded azotized principles of the animal and vegetable kingdoms, which, when left to putrefactive change, or subjected to destructive distillation, almost invariably give rise to an abundant production of this substance.

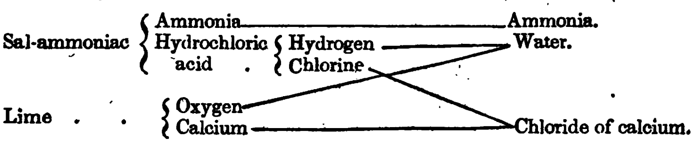
The analysis of ammoniacal gas is easily effected. When a portion is confined in a graduated tube over mercury, and electric sparks passed through it for a considerable time, the volume of the gas gradually increases until it becomes doubled. On examination the tube is found to contain a mixture of 3 measures hydrogen gas and 1 measure nitrogen. Every two volumes of the ammonia, therefore, contained three volumes of hydrogen and one of nitrogen, the whole being condensed to the extent of one-half. The weight of the two constituents will be in the proportion of 3 parts hydrogen to 14·06 parts nitrogen.

Ammonia may also be decomposed into its elements by transmission through a red-hot tube.

Solution of ammonia is a very valuable re-agent, and is employed in a great number of chemical operations, for some of which it is necessary to have it perfectly pure. The best mode of preparation is the following:—

Equal weights of sal-ammoniac and quicklime are taken; the lime is slacked in a covered basin, and the salt reduced to powder. These are mixed, and introduced into the flask employed in preparing solution of hydrochloric acid, together with just enough water to damp the mixture, and cause it to aggregate into lumps; the rest of the apparatus is arranged exactly as in the former case, with an ounce or two of water in the wash-bottle, or enough to cover the ends of the tubes, and the gas conducted afterwards into pure distilled water, artificially cooled, as before. The cork joints are made tight with wax, a little water is put into the safety-funnel, heat cautiously applied to the flask, and the whole left to itself. The disengagement of ammonia is very regular and uniform. Chloride of calcium, with excess of hydrate of lime, remains in the flask.

The decomposition of the salt is usually represented in the manner shown by the subjoined diagram.



Solution of ammonia should be perfectly colorless, leave no residue on evaporation, and when supersaturated by nitric acid, give no cloud or muddiness with nitrate of silver. Its density diminishes with its strength, that of the most concentrated being about ·875; the value in alkali of any sample of liquor ammoniæ is most safely inferred, not from a knowledge of its density, but from the quantity of acid a given amount will saturate. The mode of conducting this experiment will be found described under *Alkalimetry*.

When solution of ammonia is mixed with acids of various kinds, salts are generated, which resemble in the most complete manner the corresponding compounds of potash and soda; these are best discussed in connection with the latter. Any ammoniacal salt can at once be recognized by the evolution of ammonia when it is heated with hydrate of lime, or solution of carbonate of potash or soda.

SULPHUR, SELENIUM, AND PHOSPHORUS WITH HYDROGEN.

Sulphuretted hydrogen; hydrosulphuric acid; sulphydric acid.—There are two methods by which this important compound can be readily prepared, namely, by the action of dilute sulphuric acid upon sulphuret of iron, and by the decomposition of sulphuret of antimony by hydrochloric acid. The first method yields it most easily, and the second in the purest state.

Proto-sulphuret of iron is put into the apparatus for hydrogen, already several times mentioned, together with some water, and oil of vitriol is added by the funnel, until a copious disengagement of gas takes place. This is to be collected over tepid water. The reaction is thus explained.

Sulphuret of iron	Sulphur	Sulphuretted hydrogen.
	Iron	
Water . . .	Hydrogen	
	Oxygen	
Sulphuric acid		Sulphate of oxide of iron.

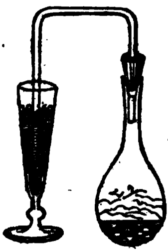
By the other plan, finely powdered sulphuret of antimony is put into a flask, to which a cork and bent tube can be adapted, and strong liquid hydrochloric acid poured upon it. On the application of heat, a double interchange occurs between the bodies present, sulphuretted hydrogen being formed, and chloride of antimony. The action only lasts while the heat is maintained.

Hydrochloric acid	Hydrogen	Sulphuretted hydrogen.
	Chlorine	
Sulphuret of antimony . . .	Sulphur	
	Antimony	Chloride of antimony.

Sulphuretted hydrogen is a colorless gas, having the odor of putrid eggs; it is most offensive when in small quantity, when a mere trace is present in the air. It is not irritating, but, on the contrary, powerfully narcotic. When set on fire, it burns with a blue flame, producing water and sulphurous acid when the supply of air is abundant, and depositing sulphur when the oxygen is deficient. Mixed with chlorine, it is instantly decomposed, with separation of the whole of the sulphur.

This gas has a specific gravity of 1·171; 100 cubic inches weigh 36·33 grains. A pressure of 17 atmospheres at 50° reduces it to the liquid form. Cold water dissolves its own volume of sulphuretted hydrogen, and the solution is often directed to be kept as a test; it is so prone to decomposition, however, by the oxygen of the air, that it speedily spoils. A much better plan is, to keep a little apparatus for generating the gas always at hand, and ready for use at a moment's notice. A small bottle or flask, to which a bit of bent tube is fitted by a cork, is supplied with a little sulphuret of iron and water; when required for use, a few drops of oil of vitriol are added, and the gas is at once evolved. The experiment completed, the liquid is poured from the bottle, replaced by a little clean water, and the instrument is again ready for use.

Fig. 115.



When potassium is heated in sulphuretted hydrogen, the metal burns with great energy, becoming converted into sulphuret, while pure hydrogen remains, equal in volume to the original gas. Taking this fact into account and comparing the density of the gas with those of hydrogen and sulphur-vapor, it appears that every volume of sulphuretted hydrogen contains one

volume of hydrogen, and one-sixth of a volume of sulphur-vapor, the whole condensed into one volume. This corresponds very nearly with its composition by weight, determined by other means, namely, 16·09 parts sulphur to 1 part hydrogen.

When a mixture is made of 100 measures of sulphuretted hydrogen and 150 measures of pure oxygen, and exploded by the electric spark, complete combustion ensues, and 100 measures of sulphurous acid gas result.

Sulphuretted hydrogen is a frequent product of the putrefaction of organic matter, both animal and vegetable; it occurs also in certain mineral springs, as at Harrowgate, and elsewhere. When accidentally present in the atmosphere of an apartment, it may be instantaneously destroyed by a small quantity of chlorine gas.

There are few re-agents of greater value to the practical chemist than this substance; when brought in contact with many metallic solutions, it gives rise to precipitates, which are often exceedingly characteristic in appearance, and it frequently affords the means also of separating metals from each other with the greatest precision and certainty. The precipitates spoken of are insoluble sulphurets, formed by the mutual decomposition of the metallic oxides or chlorides and sulphuretted hydrogen, water or hydrochloric acid being produced at the same time. All the metals are in fact, precipitated whose sulphurets are insoluble in water and in dilute acids.

Sulphuretted hydrogen possesses itself the properties of an acid; its solution in water reddens litmus paper.

The best test for the presence of this compound is paper wetted with solution of acetate of lead. The salt is blackened by the smallest trace of the gas.

Persulphuret of hydrogen.—This substance corresponds in constitution and instability to the peroxide of hydrogen; it is prepared by the following means:—

Equal weights of slaked lime and flowers of sulphur are boiled with 5 or 6 parts of water for half an hour, when a deep orange colored solution is produced, containing among other things persulphuret of calcium. This is filtered, and slowly added to an excess of dilute sulphuric acid, with constant agitation. A white precipitate of separated sulphur makes its appearance, together with a quantity of yellow oily-looking matter, which collects at the bottom of the vessel; this is persulphuret of hydrogen.*

* The reaction which ensues when hydrate of lime, sulphur and water are boiled together, is rather complex, deutosulphuret and pentasulphuret of calcium being formed, together with hyposulphite of lime, arising from the transfer of the oxygen of the decomposed lime to another portion of sulphur.

2 eq. lime { 2 eq. calcium → 2 eq. deutosulphuret of calcium.
{ 2 eq. oxygen
4 eq. sulphur
2 eq. sulphur → 1 eq. hyposulphurous acid.

The deutosulphuret of calcium decomposed by an acid under favorable circumstances, yields a salt of lime and deutosulphuret (persulphuret) of hydrogen.

1 eq. deutosulp- { 2 eq. sulphur → 1 eq. deutosulphuret of hydrogen.
calcium . . . { 1 eq. calcium
1 eq. water . . . { 1 eq. hydrogen
{ 1 eq. oxygen
Sulphuric acid → 1 eq. sulphate of lime.

When the acid is poured into the sulphuret, sulphuretted hydrogen, water and sulphate of lime are produced, while the excess of sulphur is thrown down as a fine white powder, the "precipitated sulphur" of the Pharmacopœia. When the object is to prepare the latter substance, hydrochloric acid must be used in place of sulphuric.

If the experiment be conducted by pouring the *acid* into the solution of sulphuret, then nothing but finely-divided precipitated sulphur is obtained.

The persulphuret is a yellow, viscid, insoluble liquid, exhaling the odor of sulphuretted hydrogen; its specific gravity is 1·769. It is slowly decomposed even in the cold into sulphur and sulphuretted hydrogen, and instantly by a higher temperature, or by contact with many metallic oxides. This compound probably contains twice as much sulphur in relation to the other element as sulphuretted hydrogen.

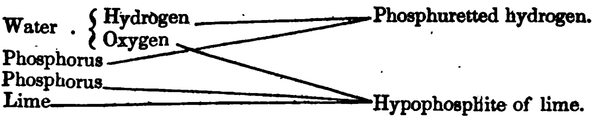
Hydrogen and selenium; seleniuretted hydrogen.—This substance is produced by the action of dilute sulphuric acid upon seleniuret of potassium or iron; it very much resembles sulphuretted hydrogen, being a colorless gas, freely soluble in water, and decomposing metallic solutions like that substance; insoluble seleniurets are thus produced. This gas is said to act very powerfully upon the lining membrane of the nose, exciting catarrhal symptoms, and destroying the sense of smell. It contains 39·57 parts selenium, and 1 part hydrogen.

Phosphorus and hydrogen; phosphuretted hydrogen.—This body bears a slight analogy in some of its chemical relations to ammoniacal gas; it is, however, destitute of alkaline properties.

Phosphuretted hydrogen may be obtained in a state of purity by heating in a small retort hydrated phosphorous acid, which is by such treatment decomposed into phosphuretted hydrogen and hydrated phosphoric acid.*

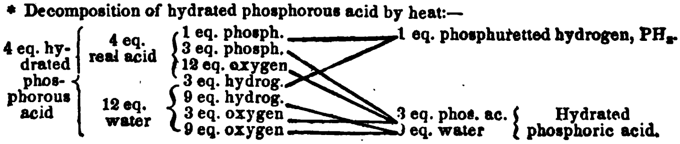
Thus obtained, the gas has a density of 1·24. It contains 31·38 parts phosphorus, and 3 parts hydrogen, and is so constituted that every two volumes contain 3 volumes of hydrogen and half a volume of phosphorous vapor, condensed into two volumes. It possesses a highly disagreeable odor of garlic, is slightly soluble in water, and burns with a brilliant white flame, forming water and phosphoric acid.

Phosphuretted hydrogen may also be produced by boiling together in a retort of small dimensions caustic potash or hydrate of lime, water, and phosphorus; the vessel should be filled to the neck, and the extremity of the latter made to dip into the water of the pneumatic trough. In the reaction which ensues the water is decomposed, and both its elements combine with the phosphorus. The alkali acts by *its presence* determining the decomposition of the water, in the same manner as sulphuric acid determines the decomposition of water when in contact with zinc.



The phosphuretted hydrogen prepared by the latter process has the singular property of spontaneous inflammability when admitted into the air or into oxygen gas; with the latter, the experiment is very beautiful, but requires caution; the bubbles should be singly admitted. When kept over water for some time, the gas loses this property, without otherwise suffering any appre-

* Decomposition of hydrated phosphorous acid by heat:—



ciable change; but if dried by chloride of calcium, it may be kept unaltered for a much longer period. Charcoal and other porous absorbents destroy the spontaneous inflammability of the gas, and the same effect is produced by a minute quantity of several combustible bodies, as the vapor of potassium and of ether or essential oil. The property is *conferred* upon phosphuretted hydrogen from either source, by the addition of an exceedingly small quantity of nitrous acid vapor.* The effect is no doubt due to the presence of a trace of some phosphorus-compound, possibly an oxide, which has not yet been isolated.† Phosphuretted hydrogen decomposes several metallic solutions, giving rise to precipitates of insoluble phosphurets. With hydriodic acid it forms a crystalline compound, somewhat resembling sal-ammoniac.

Nitrogen with chlorine and iodine; chloride of nitrogen.—When sal-ammoniac or nitrate of ammonia is dissolved in water, and a jar of chlorine gas inverted into the solution, the gas is absorbed, and a deep yellow oily liquid is observed to collect upon the surface of the solution, which ultimately sinks in globules to the bottom. This is chloride of nitrogen, the most dangerously-explosive substance known. The following is the safest method of conducting the experiment:—

A somewhat dilute and tepid solution of pure sal-ammoniac in distilled water is poured into a clean basin, and a bottle of chlorine, the neck of which is quite free from grease, inverted into it. A shallow and heavy leaden cup is placed beneath the mouth of the bottle to collect the product. When enough has been obtained, the leaden vessel may be withdrawn with its dangerous contents, the chloride remaining covered with a stratum of water. The operator should protect his face with a strong wire-gauze mask when experimenting upon this substance.

The change is explained by the following diagram:

Chlorine ——— Chloride of nitrogen.
Chlorine ——— Hydrochloric acid.
Sal-ammoniac { Nitrogen, Hydrogen } Hydrochloric acid ——— Hydrochloric acid.

Chloride of nitrogen is very volatile, and its vapor is exceedingly irritating to the eyes. It has a specific gravity of 1·653. It may be distilled at 160°, although the experiment is attended with great danger. Between 200° and 212° it explodes with the most fearful violence. Contact with almost any combustible matter, as oil or fat of any kind, determines the explosion at common temperatures; a vessel of porcelain, glass, or even of cast-iron, is broken to pieces, and the leaden cup receives a deep indentation. This body has usually been supposed to contain nitrogen and chlorine in the proportions of

* Graham, Elements, p. 298.

† Phosphorus and hydrogen are admitted to combine in three proportions (Leverrier, An. de Ch. and Ph., lx. 174), forming a solid phosphuretted hydrogen (PH), a spontaneously inflammable phosphuretted hydrogen (PH_2), and a gaseous phosphuretted hydrogen. The solid phosphuretted hydrogen is deposited when the gaseous compound (PH_3) is exposed to the sun's rays. It is a yellow powder, insoluble in water, and decomposable by heat.

The spontaneously inflammable phosphuretted hydrogen is liquid below 50°, colorless and transparent, very inflammable. (P. Thenard, Rev. Scientif. Aout, 1844.) It accompanies the gaseous compound in the amount of about one-thirtieth of its volume, and communicates to it the spontaneous inflammability. The loss of this property on exposure to light is explained by the spontaneously inflammable compound (PH_2), being decomposed into solid phosphuretted hydrogen (PH), which is deposited, and gaseous phosphuretted hydrogen (PH_3). The gaseous phosphuretted hydrogen is noticed in the text, contaminated, however, with one-thirtieth of its volume of the spontaneously inflammable compound. It may be obtained pure by acting on phosphuret of lime with fuming hydrochloric acid; by a slight heat it is liberated in the gaseous state.—R. B.

14·06 parts of the former to 106·23 parts of the latter, but recent experiments upon the corresponding iodine-compound induce a belief that it contains hydrogen.*

Iodide of nitrogen.—When finely-powdered iodine is put into caustic ammonia it is in part dissolved, giving a deep brown solution, and the residue is converted into a black powder, which is the substance in question. The brown liquid consists of hydriodic acid holding iodine in solution, and is easily separated from the solid product by a filter. The latter while still wet is distributed in small quantities upon separate pieces of bibulous paper, and left to dry in the air.

Iodide of nitrogen is a black insoluble powder, which, when dry, explodes with the slightest touch, even that of a feather; and sometimes without any obvious cause. The explosion is not nearly so violent as that of the compound last described, and is attended with the production of violent fumes of iodine.

OTHER COMPOUNDS OF NON-METALLIC ELEMENTS.

Chlorine with sulphur and phosphorus.—Chloride of sulphur.—This compound is easily prepared by passing dry chlorine over the surface of sulphur kept melted in a small glass retort connected with a good condensing arrangement. The chloride distils over as a deep orange-yellow mobile liquid, of peculiar and disagreeable odour, which boils at 280°. As this substance dissolves both sulphur and chlorine, it is not easy to obtain it in a pure and definite state. It contains 32·18 parts sulphur and 35·41 parts chlorine.†

Chloride of sulphur is instantly decomposed by water; hydrochloric and hyposulphurous acids are formed, and sulphur separated. The hyposulphurous acid in its turn decomposes into sulphur and sulphurous acids.

Chlorides of phosphorus.—Terchloride.‡—This is prepared in the same manner as chloride of sulphur, by gently heating phosphorus in dry chlorine gas, the phosphorus being in excess. Or, by passing the vapor of phosphorus over fragments of calomel (sub-chloride of mercury) contained in a glass tube and strongly heated. It is a colorless, thin liquid, which fumes in the air, and possesses a powerful and offensive odor. Its specific gravity is 1·45. Thrown into water, it sinks to the bottom of that liquid, and becomes slowly decomposed, yielding phosphorous acid and hydrochloric acid. This compound contains 31·38 parts phosphorus and 106·23 parts chlorine.

Perchloride of phosphorus.§—The compound formed when phosphorus is burned in excess of chlorine. Into a large retort, fitted with a cap and stopcock, pieces of phosphorus are introduced; the retort is then exhausted, and filled with dry chlorine gas. The phosphorus takes fire and burns with a pale flame, forming a white, volatile, crystalline sublimate, which is the perchloride. It may be obtained in larger quantity by passing a stream of dry chlorine gas into the preceding liquid chloride, which becomes gradually converted into a solid, crystalline mass. Perchloride of phosphorus is decomposed by water, yielding phosphoric and hydrochloric acids.

Chlorine and carbon.—Three compounds of chlorine and carbon are known to exist. One of them is obtained indirectly by the action of chlorine upon certain organic compounds, and the two others are derived from the decomposition by heat of the first. They are described in connection with the history of alcohol.

Iodine with sulphur and phosphorus.—These compounds are formed by gently heating together the materials in vessels from which the air is excluded. They

* Instead of NCl_3, it may in reality be NH_2+Cl, or chloride of *amidogen*.
† S_2Cl. ‡ PCl_3. § PCl_5.

present few points of interest. The iodides of phosphorus, prepared in this manner, are fusible, crystalline substances, which decompose by contact with water, and yield hydriodic acid and phosphorus, or phosphoric acid.

Chlorine with iodine.—Iodine readily absorbs chlorine gas, forming when the chlorine is in excess, a solid, yellow compound, and when the iodine preponderates, a brown liquid. The solid iodide is decomposed by water, yielding hydrochloric and iodic acids.*

Another definite compound is formed by heating in a retort a mixture of 1 part iodine and 4 parts chlorate of potash; oxygen gas and chloride of iodine are disengaged, and the latter may be condensed by suitable means. Iodate and hyperchlorate of potash remain in the retort.

This chloride of iodine is a yellow, oily liquid, of suffocating smell and astringent taste; it is soluble in water and alcohol without decomposition. It probably consists of 126·36 parts iodine, and 35·41 parts chlorine.†

Carbon and sulphur.—Bisulphuret of carbon.—A wide porcelain tube is filled with pieces of charcoal which have been recently heated to redness in a covered crucible, and fixed across a furnace in a slightly inclined position. Into the lower extremity a tolerably wide tube is secured by the aid of a cork; this tube bends downwards and passes nearly to the bottom of a bottle filled with fragments of ice and a little water. The porcelain tube being heated to bright redness, fragments of sulphur are thrown into the open end, which is immediately afterwards stopped by a cork. The sulphur melts and becomes converted into vapor, which, at that high temperature, combines with the carbon, forming an exceedingly volatile compound, which is condensed by the ice and collects at the bottom of the vessel. This is collected and re-distilled with very gentle heat in a retort connected with a good condenser. Bisulphuret of carbon is a transparent colorless liquid of great refractive and dispersive power. Its density is 1·272. It boils at 110° F., and emits vapor of considerable elasticity at common temperatures. The odor of this substance is very repulsive. When set on fire in the air it burns with a blue flame, forming carbonic acid and sulphurous acid gases, and when its vapor is mixed with oxygen it becomes explosive.

It freely dissolves sulphur, and by spontaneous evaporation deposits the latter in beautiful crystals.

* Hence it doubtless contains 1 eq. iodine, and 5 eq. chlorine, or $I\,Cl_5$.

† Or single equivalents.

ON THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY.

The study of the non-metallic elements can be pushed to a very considerable extent, and a large amount of precise and exceedingly important information acquired, without much direct reference to the great fundamental laws of chemical union; the subject cannot be discussed in this manner completely, as will be obvious from occasional cases of anticipation in many of the foregoing foot-notes; still much may be done by this simple method of proceeding. The bodies themselves, in their combinations, furnish admirable illustrations of the general laws referred to, but the study of their leading characters and relations does not of necessity involve a previous knowledge of these laws themselves.

It is thought that by such an arrangement, the comprehension of these very important general principles may become in some measure facilitated by constant references to examples of combinations, the elements and products of which have been already described. So much more difficult is it to gain a clear and distinct idea of any proposition of great generality from a simple enunciation, than to understand the bearing of the same law when illustrated by a single good and familiar instance.

Before proceeding further, however, it is absolutely necessary that these matters should be discussed; the metallic compounds are so numerous and complicated, that the establishment of some general principle, some connecting link, becomes indispensable. The doctrine of equivalents, and the laws which regulate the formation of saline compounds, supply this deficiency.

In the organic department of the science, the most interesting perhaps of all, a knowledge of these principles, and further, an acquaintance or even familiarity with the beautiful system of chemical notation now in use, are absolutely required. This latter is found of very great service in the study of salts and other complex inorganic compounds, but in that of organic chemistry it cannot be dispensed with.

It will be proper to commence with a simple statement of four great fundamental laws of chemical union; the only laws in fact which have yet been shown to hold good universally—

The laws of combination.

1. All chemical compounds are definite in their nature, the ratio of the elements being constant.

2. When any body is capable of uniting with a second in several proportions, these proportions bear a simple relation to each other.

3. If a body, A, unite with other bodies B, C, D, the quantities of B, C, D, which unite with A, represent the *relations in which they unite among themselves*, in the event of union taking place.

4. The combining quantity of a compound is the sum of the combining quantities of its components.

(1.) *Constancy of composition.*—That the same chemical compound invariably contains the same elements uuited in unvarying proportions, is a propo-

sition almost axiomatic; it is involved in the very idea of identity itself. The converse, however, is very far from being true; the same elements combining in the same proportions do not of necessity generate the same substance.

Organic chemistry furnishes numerous instances of this very remarkable fact, in which the greatest diversity of properties is associated with identity of chemical composition. These cases seem to be confined to organic chemistry; no well-established and undoubted example being known in the inorganic or mineral division of the science.

(2.) *Multiple proportions.*—Illustrations of this simple and beautiful law abound on every side; let the reader take for example the compounds of nitrogen and oxygen, five in number, containing the proportions of the two elements so described that the quantity of one of them shall remain constant—

	Nitrogen.	Oxygen.
Protoxide	14·06	8
Deutoxide	14·06	16
Hyponitrous acid	14·06	24
Nitrous acid	14·06	32
Nitric acid	14·06	40

It will be seen at a glance, that while the nitrogen remains the same, the quantities of oxygen increase by *multiples of* 8, or the number representing the quantity of that substance in the first compound; thus 8, 8×2, 8×3, 8×4, and 8×5 give respectively the oxygen in the protoxide, the deutoxide, hyponitrous acid, nitrous acid, and lastly, nitric acid. Again, carbonic acid contains exactly twice as much oxygen in proportion to the other constituent as carbonic oxide; the peroxide of hydrogen is twice as rich in oxygen as water; the corresponding sulphurets exhibit the same phenomena, while the metallic compounds offer one continued series of illustrations of the law, although the ratio is not always so simple as that of 1 to 2.

It often happens that one or more members of a series are yet deficient; the oxides of chlorine afford a good example.

	Chlorine.	Oxygen.
Hypochlorous acid	35·41	8
Chlorous acid	35·41	32
Chloric acid	35·41	40
Hyperchloric acid	35·41	56

Here the quantities of oxygen progress in the following order:—8, 8×4, 8×5, 8×7; gaps are manifest between the first and second substances, and between the third and fourth; these remain to be filled up by future researches. The existence of a simple relation among the numbers in the second column is, however, not the less evident. Even when difficulties seem to occur in applying this principle, they are only apparent, and vanish when closely examined. In the highly complex sulphur-series, given at p. 113, the numbers placed in each column are multiples of the lowest among them, and by making the assumption, which is not at all extravagant, that the two last named bodies are combinations of hyposulphuric acid and sulphur, we may arrange the four direct compounds in such a manner that the sulphur shall remain a constant quantity.

	Sulphur.	Oxygen.
Hyposulphurous acid	32·18	16
Sulphurous acid	32·18	32
Hyposulphuric acid	32·18	40
Sulphuric acid	32·18	48

Compound bodies of all kinds are also subject to the law of multiples when they unite among themselves, or with elementary substances. There are two sulphates of potash and soda: the second contains twice as much acid in relation to the alkaline base as the first. There are three oxalates of potash, namely, the simple oxalate, the binoxalate, and the quadroxalate; the second has equally twice as much acid as the first, and the third twice as much as the second. Many other cases might be cited, but the student, once in possession of the principle, will easily notice them as he proceeds.

(3.) *Law of equivalents.*—It is highly important that the subject now to be discussed should be completely understood.

Let a substance be chosen whose range of affinity and powers of combination are very great, and whose compounds are susceptible of rigid and exact analysis; such a body is found in oxygen, which is known to unite with all the elementary substances, with the single exception of fluorine. Now, let a series of exact experiments be made to determine the proportion in which the different elements combine with one and the same constant quantity of oxygen, which, for reasons hereafter to be explained, may be assumed to be 8 parts by weight; and let these numbers be arranged in a column opposite the names of the substances. The result is a table or list like the following, but of course much more extensive when complete.

Oxygen	8
Hydrogen	1
Nitrogen	14·06
Carbon	6
Sulphur	16·09
Phosphorus	31·38
Chlorine	35·41
Iodine	126·36
Potassium	39·19
Iron	27·14
Copper	31·6
Lead	103·56
Silver	108·12
&c., &c.	

Now the law in question is to this effect: If such numbers represent the proportions in which the different elements combine with the arbitrarily fixed quantity of the starting-substance, the oxygen, they also represent the *proportions in which they unite among themselves*, or at any rate bear some exceedingly simple ratio to those proportions.

Thus hydrogen and chlorine combine invariably in the proportions 1 and 35·41; hydrogen and sulphur, 1 to 16·09; chlorine and silver, 35·41 to 108·12; iodine and potassium, 126·36 parts of the former to 39·19 of the latter, &c. This rule is never departed from in any one instance.

The term *equivalent* is applied to these numbers for a reason which will now be perfectly intelligible; they represent quantities capable of exactly replacing each other in combination: 1 part of hydrogen goes as far in combining with or saturating a certain amount of oxygen as 27·14 parts of iron, 39·19 of potassium, or 108·12 of silver; for the same reason, the numbers are said to represent *combining quantities*, or *proportionals*.

Nothing is more common than to speak of so many equivalents of this or

that substance being united to one or more equivalents of a second; by this expression, quantities are meant just so many times greater than these relative numbers. Thus sulphuric acid is said to contain one equivalent of sulphur, and three equivalents of oxygen; that is, a quantity of the latter, represented by three times the combining number of oxygen; phosphoric acid is made up of 1 equivalent of phosphorus and 5 oxygen; the red oxide of iron contains, as will be seen hereafter, 3 equivalents of oxygen to every 2 equivalents of metal, &c. It is an expression which will henceforward be freely and constantly employed; it is hoped, therefore, that it will be understood. The nature of the law will easily show that the choice of the body destined to serve for a point of departure is perfectly arbitrary, and regulated by considerations of convenience alone.

A body may be chosen which refuses to unite with a great number of the elements, and yet the equivalents of the latter admit of being determined by indirect means, in virtue of the very peculiar law under discussion. Oxygen does not unite with fluorine, yet the equivalent of the latter can be found by observing the quantity which combines with the *equivalent* quantity of hydrogen or calcium, already known. We may rest assured that if an oxide be ever discovered, its elements will be associated in the ratio of 8 to 18·7, or in numbers which are either multiples or sub-multiples of these.

The number assigned to the starting-substance is also equally arbitrary; if, in the table given, oxygen instead of 8 were made 10, or 100, or even a fractional number, it is quite obvious that although the other numbers would all be different, the *ratio*, or proportion among the whole, would remain unchanged, and the law would still be maintained in all its integrity.

There are in fact two such tables in use among chemists; one in which oxygen is made=8, and a second in which it is made=100; the former is generally used in this country, and the latter on the continent. The only reason for giving, as in the present volume, a preference to the first is, that the numbers are smaller and more easily remembered.

The number 8 has been chosen in this table to represent oxygen from an opinion long held by a very eminent English chemist, and recently to appearance substantiated in some remarkable instances by very elaborate investigation, that the equivalents of all bodies are multiples of that of hydrogen; and consequently, by making the latter unity, the numbers would be all integers. The question must be considered as altogether unsettled. A great stumbling-block to such a view is presented by the case of chlorine, which certainly seems to be a fractional number; and one single well-established exception will be fatal to the hypothesis.

As all experimental investigations are attended with a certain amount of error, the results contained in the following table must be looked upon merely as good approximations to the truth. For the same reason, small differences are often observed in the determination of the equivalents of the same bodies by different experimenters, of which some notice will be found in the Appendix.

TABLE OF ELEMENTARY SUBSTANCES, WITH THEIR EQUIVALENTS.

	Oxy.=8.	Oxy.=100.		Oxy.=8.	Oxy.=100.
Aluminium	13·69	171·17	Mercury	101·27	1265·82
Antimony	129·04	1612·90	Molybdenum	47·88	598·52
Arsenic	75·21	940·08	Nickel	29·57	369·68
Barium	68·55	856·88	Nitrogen	14·06	175·75
Bismuth	70·95	886.97	Osmium	99·56	1244·49
Boron	10·90	136·20	Oxygen	8·	100·
Bromine	78·26	978·31	Palladium	53·27	665·90
Cadmium	55·74	696·77	Phosphorus	31·38	392·28
Calcium	20·	250·	Platinum	98·68	1233·50
Carbon	6·	75·	Potassium	39·19	489·92
Cerium	45·98	574·70	Rhodium	52·11	651·39
Chlorine	35·41	442·65	Selenium	39·57	494·58
Chromium	28·14	351·82	Silicon	22·18	277·31
Cobalt	29·52	368·99	Silver	108·12	1351·61
Columbium	184·59	2307·43	Sodium	23·27	290·90
Copper	31·65	395·70	Strontium	43·78	547·29
Fluorine	18·70	233·80	Sulphur	16·09	201·17
Glucinum	26·50	331·26	Tellurium	64·14	801·76
Gold	99·44	1243·	Thorium	59·59	744·90
Hydrogen	1·	12·5	Tin	58·82	735·29
Iodine	126·36	1579·50	Titanium	24·29	303·66
Iridium	98·68	1233·50	Tungsten	94·64	1183·
Iron	27·14	339·21	Vanadium	68·55	856·89
Lantanum			Uranium	60·	750·
Lead	103·56	1294·50	Yttrium	32·20	402·51
Lithium	6·43	80·33	Zinc	33·00	412·50
Magnesium	12·67	158·35	Zirconium	33·62	420·20
Manganese	27·67	345·89			

(4.) *Combining numbers of compounds.*—The law states that the equivalent or combining number of a compound is always the sum of the equivalents of its components. This is also a great fundamental truth, which it is necessary to place in a clear and conspicuous light. It is a separate and independent law, established by direct experimental evidence, and not deducible from either of the preceding.

The method of investigation by which the equivalent of a simple body is determined, has been already explained; that employed in the case of a compound is in no wise different. Take the example of the acids and alkalies as being the most explicit, and at the same time most important. An acid and a base, combined in certain definite proportions, *neutralize*, or mark each other's properties completely, and the result is a salt; these proportions are called the equivalents of the bodies, and they are very variable. Some have very high capacities of saturation, of others a much larger quantity must be employed to neutralize the same amount of base; the bases themselves present also similar phenomena. Thus, to saturate 47·19 parts of potash, or 116·12 parts of oxide of silver, there are required

40·09 parts sulphuric acid,
54·06 " nitric acid,
75·41 " chloric acid,
166·36 " iodic acid,
51· " acetic acid.

Numbers very different, but representing quantities which replace each other in combination. Now, if a quantity of some base, such as potash, be taken, which is represented by the sum of the equivalents of potassium and oxygen, then the quantity of any acid requisite for its neutralization, as determined by direct experiment, will always be found equal to the sum of the equivalents of the different components of the acid itself.

39·19	=	equivalent of potassium.
8·	=	" oxygen.
47·19	=	assumed equivalent of potash.

47·19 parts of potash are found to be exactly neutralized by 40·09 parts of real sulphuric acid, or by 54·06 parts of real nitric acid. These quantities are evidently made up by adding together the equivalent of their constituents:—

1 equiv. sulphur	= 16·09		1 equiv. nitrogen	= 14·06
3 " oxygen	= 24·		5 " oxygen	= 40·
1 " sulphuric acid	= 40·09		1 " nitric acid	= 54·06

And the same is true if any acid be taken, and the quantities of different bases required for its neutralization determined; the combining number of the compound will always be found to be the sum of the combining numbers of its components, however complex the substance may be. Even among such bodies as the vegeto-alkalies of organic chemistry, the same universal rule holds good. When salts combine, which is a thing of very common occurrence, as will hereafter be seen, it is always in the ratio of the equivalent numbers. Apart from hypothetical considerations, no *à priori* reason can be shown why such should be the case; it is, as before remarked, an independent law, established like the rest, by experiment.

A curious observation was very early made to this effect:—If two neutral salts which decompose each other when mixed, be brought in contact, the new compounds resulting from their mutual decomposition will also be neutral. For example, when solution of nitrate of baryta and sulphate of potash are mingled, they both suffer decomposition, sulphate of baryta and nitrate of potash being simultaneously formed, both of which are perfectly neutral. The reason of this will be at once evident; interchange of elements can only take place by the displacement of equivalent quantities of matter on either side. For every 54·06 parts of nitric acid set free by the decomposition of the barytic salt, 47·19 parts of potash are abandoned by the 40·09 parts of sulphuric acid with which they were previously in combination, now transferred to the baryta. But 54·06 and 47·19 are the representatives of combining quantities; hence the new compound must be neutral.

Combination by volume.—When gaseous bodies combine, it is always by measures or volumes which bear a simple relation to each other. The cause of this curious and highly interesting fact may thus be traced.

8 grains of oxygen occupy at 60° and 30 in. barom.	23·3 cubic in.
1 grain of hydrogen	46·7
35·41 grains of chlorine	46·2
126·36 grains of iodine vapor (would measure) .	46·7

The last three numbers of the second column, representing volumes, are evidently the same, allowing for slight inevitable errors of experiment, and are the double of the first; the weights to which they correspond are the equivalent weights. Hence a relation exists between the specific gravity of a gas or vapor and its combining number by weight, of such a nature that combination *necessarily* takes place among bodies of this class by measures which have a simple proportion among themselves. The many cases of gaseous combination already mentioned in the description of the non-metallic elements and their compounds, are strictly in point; oxygen with hydrogen and chlorine; hydrogen with sulphur and phosphorus; oxygen with nitrogen, &c. &c.

Compound gases behave in the same manner; ammonia and hydrochloric acid gases unite in equal volumes; chlorine and heavy carburetted hydrogen afford another example; even with the vapors of complicated organic liquids the same fact is constantly observed.

This relation between density and combining number is admirably shown by the following table, embracing a few cases, in which the two are placed side by side, hydrogen being taken as unity.

	Density.	Equal.	Combining volumes.
Hydrogen	1·	1·	1
Nitrogen	14·03	14·06	1
Chlorine	35·64	35·41	1
Bromine vapor	78·	78·26	1
Iodine vapor	126·	126·36	1
Oxygen	16·	8·	½
Phosphorus vapor	62·	31·38	½
Arsenic vapor	150.	75·21	½
Sulphur vapor	96·	16·09	⅙
Mercury vapor	101·	101·27	1

This law often serves to check and corroborate the results of experimental investigation, and is consequently of great practical utility.

There is an expression sometimes made use of in chemical writings which it is necessary to explain, namely, the meaning of the words *hypothetical density of vapor*, applied to a substance which has never been volatilized, such as carbon, whose real specific gravity in that state must of course be unknown; it is easy to understand the origin of this term. Carbonic acid contains a volume of oxygen equal to its own; consequently, if the specific gravity of the latter be subtracted from that of the former gas, the residue will express the proportion borne by the weight of the carbon, certainly then in a vaporous state, to that of the two gases.

The specific gravity of carbonic acid is	1·5240
That of oxygen is	1·1057
	·4183

On the supposition that carbonic acid contains equal volumes of oxygen and this vapor of carbon, condensed to one-half, the latter will have the density represented by ·4183. But this is merely a supposition, a guess; no proof can be given that carbonic acid gas is so constituted. All that can be safely said is contained in the prediction, that should the specific gravity of the vapor of carbon ever be determined, it will be found to coincide with this number, or to bear some simple and obvious relation to it.

Such is a brief account of the great laws by which chemical combinations, of every kind, are governed and regulated; and it cannot be too often repeated that the discovery of these beautiful lawsh as been the result of pure experimental inquiry. They have been established on this firm and stable foundation by the joint labors of very many illustrious men; they are the expression of fact, and are totally independent of all hypotheses or theories whatsoever.

Chemical notation; symbols.—For convenience in communicating ideas respecting the composition, and supposed constitution, of chemical compounds, and explaining in a clear and simple manner the results or changes they may happen to undergo, recourse is had to a kind of written symbolical language, the principle of which must now be explained. To represent compounds by symbols is no novelty, as the works of the Alchemists will show, but these have been mere arbitrary marks or characters invented for the sake of brevity, or sometimes perhaps for that of obscurity.

The plan about to be described is due to Berzelius; it has been adopted, with slight modifications, wherever chemistry is pursued.

Every elementary substance is designated by the first letter of its Latin name, in capital, or by the first letter conjoined with a second small one, the most characteristic in the word, as the names of many bodies begin alike. The single letter is usually confined to the earliest discovered, or most important element. Further, by a most ingenious idea, the symbol is made to represent not the substance in the abstract, but *one equivalent of that substance.*

Table of symbols of the elementary bodies.

Aluminum	Al	Mercury (Hydrargyrum)	Hg
Antimony (Stibium)	Sb	Molybdenum	Mo
Arsenic	As	Nickel	Ni
Barium	Ba	Nitrogen	N
Bismuth	Bi	Osmium	Os
Boron	B	Oxygen	O
Bromine	Br	Palladium	Pd
Cadmium	Cd	Phosphorus	P
Calcium	Ca	Platinum	Pt
Carbon	C	Potassium (Kalium)	K
Cerium	Ce	Rhodium	R
Chlorine	Cl	Selenium	Se
Chromium	Cr	Silicon	Si
Cobalt	Co	Silver (Argentum)	Ag
Columbium	Ta	Sodium (Natrium)	Na
Copper (Cuprum)	Cu	Strontium	Sr
Fluorine	F	Sulphur	S
Glucinum	G	Tellurium	Te
Gold (Aurum)	Au	Thorium	Th
Hydrogen	H	Tin (Stannum)	Sn
Iodine	I	Titanium	Ti
Iridium	Ir	Tungsten (Wolframium)	W
Iron (Ferrum)	Fe	Vanadium	V
Lantanum	Ln	Uranium	U
Lead (Plumbum)	Pb	Yttrium	Y
Lithium	L	Zinc	Zn
Magnesium	Mg	Zirconium	Zr
Manganese	Mn		

Combination between bodies in the ratio of the equivalents is expressed by mere juxtaposition of the symbols, or sometimes by interposing the sign of addition. For example:

Water . . .	HO, or $H+O$
Hydrochloric acid	HCl, or $H+Cl$
Protoxide of iron	FeO, or $Fe+O$.

When more than one equivalent is intended, a suitable number is added, sometimes being placed before the symbol, like a co-efficient in algebra, sometimes appended after the manner of an exponent, but more commonly placed a little below on the right.

Peroxide of hydrogen	$H+2O$, or HO_2, or HO_2
Sulphuric acid . .	$S+3O$, or SO^3, or SO_3
Hyposulphuric acid	$2S+5O$, or S^2O^5, or S_2O_5.

Combination between bodies themselves compound, is indicated by the sign of addition, or by a comma. When both are used in the same formula, the latter may be very conveniently applied, as Professor Graham has suggested, to indicate the closest and most intimate union. A number standing before symbols enclosed within a bracket, signifies that the whole of the latter are to be multiplied by that number. Occasionally the bracket is omitted, when the number affects all the symbols between itself and the next sign. A few examples will serve to illustrate these several points.

Sulphate of soda	$NaO+SO_3$, or NaO, SO_3
Nitrate of potash	$KO+NO_5$, or KO, NO_5.

The base being always placed first.

Double sulphate of copper and potash	CuO, SO_3+KO, SO_3
The same in a crystallized state	CuO, SO_3+KO, SO_3+6HO.

Common crystallized alum, or double sulphate of alumina and potash, is thus written—

$$Al_2O_3, 3SO_3+KO, SO_3+24HO.$$

In expressing organic compounds, where three or more elements exist, the same plan is used.

Sugar .	$C_{12}H_{11}O_{11}$
Alcohol	$C_4H_6O_2$
Acetic acid	$C_4H_3O_3$
Morphia	$C_{35}H_{20}N\ O_6$
Acetate of morphia	$C_{35}H_{20}N\ O_6, C_4H_3O_3$
Acetate of soda . .	$NaO, C_4H_3O_3$.

By such a system, the eye is enabled to embrace the whole at a glance, and gain a distinct idea of the composition of the body and its relations to others similarly described.

Some authors are in the habit of making use of contractions, which, however, are by no means generally adopted. Thus, two equivalents of a substance are indicated by the symbol with a short line drawn through or below it; an equivalent of oxygen is signified by a dot, and one of sulphur by a

comma. These alterations are sometimes convenient for abbreviating a long formula, but easily liable to mistakes. Thus,

Peroxide of iron $\underline{Fe}\,O_3$, or $\dddot{\underline{Fe}}$, instead of Fe_2O_3

Bisulphuret of Carbon $\ddot{C}$, instead of CS_2

Crystallized alum at above $\dddot{\underline{Al}}\,\bar{S}_3+\ddddot{K}S+24\dot{H}$.

The Atomic Theory.

That no attempt should have been made to explain the reason of the very remarkable manner in which combination occurs in the production of chemical compounds, and to point out the nature of the relations between the different modifications of matter which fix and determine these peculiar and definite changes, would have been unlikely, and in contradiction with the speculative tendency of the human mind. Such an attempt, and a very ingenious and successful one it is, has been made, namely, the atomic hypothesis of Dr. Dalton.

From very ancient times, the question of the constitution of matter with respect to divisibility has been debated, some adopting the opinion that this divisibility is infinite, and others, that when the particles become reduced to a certain degree of tenuity, far indeed beyond any state that can be reached by mechanical means, they cease to be further diminished in magnitude; they become, in short, *atoms.** Now, however the imagination may succeed in figuring to itself the condition of matter on either view, it is hardly necessary to mention that we have absolutely no means at our disposal for deciding such a question, which remains at the present day in the same state as when it first engaged the attention of the Greek philosophers, or perhaps that of the sages of Egypt and Hindostan long before them.

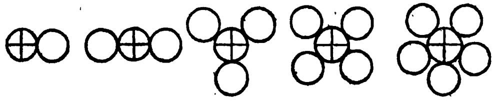
Dr. Dalton's hypothesis sets out by assuming the existence of such atoms or indivisible particles, and states, that compounds are formed by the union of atoms of different bodies one to one, one to two, &c. The compound atom joins itself in the same manner to a compound atom of another kind, and a combination of the second order results. Let it be granted further, that the relative weights of the atoms are in the proportions of the equivalent numbers, and the hypothesis becomes capable of rendering consistent and satisfactory reasons for all the consequences of those beautiful laws of combination lately discussed.

Chemical compounds must always be definite; they must always contain the same number of atoms, of the same kind, arranged in a similar manner. The same kind and number of atoms need not, however, of necessity produce the same substance, for they may be differently arranged; and much depends upon this circumstance.

Again, the law of multiple proportions is perfectly well explained; an atom of nitrogen unites with one of oxygen to form laughing gas; with two, to form binoxide of nitrogen; with three, to produce hyponitrous acid; with four, nitrous acid; and with five, nitric acid,—perhaps something after the manner represented, (fig. 116.,) in which the circle with a cross represents the atom of nitrogen, and the plain circle that of oxygen.

* Ατομος, that which cannot be cut.

Fig. 116.



Two atoms of one substance may unite themselves with three or even with seven of another, as in the case of one of the acids of manganese, but such combinations are rare.

The mode in which bodies replace, or may be substituted for each other, is also perfectly intelligible, as a little consideration will show.

Finally, the law which fixes the equivalent of a compound at the sum of the equivalents of the components, receives an equally satisfactory explanation.

The difficulties in the general application of the atomic hypothesis are chiefly felt in attempting to establish some wide and universal relation between combining number and combining volume, among gases and vapors, and in the case of the highly complex products of organic chemistry. These obstacles have grown up in comparatively recent times. On the other hand, the remarkable observations of the specific capacities for heat of equivalent quantities of the solid elementary substances, might be urged in favor of this or some similar molecular hypothesis. But even here serious discrepancies exist; we may not take liberties with equivalent numbers determined by exact chemical research, and in addition, all simple relation is found to be wanting between the capacity for heat of the compound and that of its elements.

The theory in question has rendered great service to chemical science; it has excited a vast amount of inquiry and investigation which have contributed very largely to define and fix the laws of combination themselves. In more recent days it is not impossible that without some such hypothetical guide the exquisitely beautiful relations which Mitscherlich and others have shown to exist between crystalline form and chemical composition, might never have been brought to light, or, at any rate, their discovery might have been greatly delayed. At the same time, it is indispensable to draw the broadest possible line of distinction between this, which is at the best but a graceful, ingenious, and, in its place, useful hypothesis, and those great general laws of chemical action which are the pure and unmixed result of inductive research.*

Chemical Affinity.

The term chemical affinity, or chemical attraction, has been invented to describe that particular power or force, in virtue of which, union, often of a very intimate and permanent nature, takes place between two or more bodies, in such a way as to give rise to a *new* substance, having for the most part properties completely in discordance with those of its components.

The attraction thus exerted between different kinds of matter is to be distinguished from other modifications of attractive force which are exerted

* The expression *atomic* weight is very often substituted for that of *equivalent* weight, and is, in fact, in almost every case to be understood as such: it is, perhaps, better avoided.

indiscriminately between all descriptions of substances, sometimes at enormous distances, and sometimes at intervals quite inappreciable. Examples of the latter are to be seen in cases of what is called *cohesion*, when the particles of solid bodies are immovably bound together into a mass. Then there are other effects of, if possible, a still more obscure kind; such as the various actions of surface, the adhesion of certain liquids to glass, the repulsion of others, the ascent of water in narrow tubes, and a multitude of curious phenomena which are described in works on Natural Philosophy, under the head of *molecular actions*. From all these true chemical attraction may be at once distinguished by the deep and complete change of characters which follows its exertion; we might define affinity to be a force by which new substances are generated.

It seems to be a general law that bodies most opposed to each other in chemical properties evince the greatest tendency to enter into combination, and conversely, bodies between which strong analogies and resemblances can be traced, manifest a much smaller amount of mutual attraction. For example, hydrogen and the metals tend very strongly indeed to combine with oxygen, chlorine and iodine; the attraction between the different members of these two groups is incomparably more feeble. Sulphur and phosphorus stand as it were mid-way; they combine with substances of one and the other class, their properties separating them sufficiently from both. Acids are drawn towards alkalies, and alkalies towards acids, while union among themselves rarely, if ever, takes place.

Nevertheless, chemical combination graduates so imperceptibly into mere mechanical mixture, that it is often impossible to mark the limit. Solution is the result of a weak kind of affinity existing between the substance dissolved and the solvent; an affinity so feeble as completely to lose one of its most prominent features when in a more exalted condition, namely, power of causing elevation of temperature, for in the act of mere solution the temperature falls, the heat of combination being lost and overpowered by the effects of change of state.

The force of chemical attraction thus varies greatly with the nature of the substances between which it is exerted; it is influenced, moreover, to a very large extent, by external or adventitious circumstances. An idea formerly prevailed that the relations of affinity were fixed and constant between the same substances, and great pains were taken in the preparation of tables exhibiting what was called the precedence of affinities. The order pointed out in these lists is now acknowledged to represent the order of precedence *for the circumstances* under which the experiments were made, but nothing more; so soon as these circumstances become changed, the order is disturbed. The ultimate effect, indeed, is not the result of the exercise of one single force, but rather the joint effect of a number, so complicated and so variable in intensity, that it is seldom possible to predict the consequences of any yet untried experiment. The following may serve as examples of the tables alluded to; the first illustrates the relative affinities of a number of bases for sulphuric acid, each decomposing the combination of the acid with the base below it; thus magnesia decomposes sulphate of ammonia; lime displaces the acid from sulphate of magnesia, &c. The salts are supposed to be dissolved in water. The second table exhibits the order of affinity for oxygen of several metals, mercury reducing a solution of silver, copper one of mercury, &c.

Sulphuric acid.	Oxygen.
Baryta,	Zinc,
Strontia,	Lead,
Potash,	Copper,
Soda,	Mercury,
Lime,	Silver.
Magnesia,	
Ammonia,	

It will be proper to examine shortly some of these extraneous causes to which allusion has been made, which modify to so great an extent the direct and original effects of the specific attractive force.

Alteration of temperature may be reckoned among these. When metallic mercury is heated nearly to its boiling point, and in that state exposed for a lengthened period to the air, it absorbs oxygen, and becomes converted into a dark red crystalline powder. This very same substance, when raised to a still higher temperature, spontaneously separates into metallic mercury and oxygen gas. It may be said, and probably with truth, that the latter change is greatly aided by the tendency of the metal to assume the vaporous state, but precisely the same fact is observed with another metal, palladium, which is not volatile at all, but which oxydates superficially at a red-heat, and again becomes reduced when the temperature rises to whiteness.

Insolubility and the power of vaporization are perhaps beyond all other disturbing causes the most potent; they interfere in almost every reaction which takes place, and very frequently turn the scale when the opposed forces do not greatly differ in energy. It is easy to give examples. When a solution of lime in hydrochloric acid is mixed with a solution of carbonate of ammonia, double interchange ensues, carbonate of lime and hydrochlorate of ammonia being generated. Here the action can be shown to be in a great measure determined by the insolubility of the carbonate of lime. Again, dry carbonate of lime, powdered and mixed with hydrochlorate of ammonia, and the whole heated in a retort, gives a sublimate of carbonate of ammonia, while chloride of calcium remains behind. In this instance, it is no doubt the great volatility of the new ammoniacal salt which chiefly determines the kind of decomposition.

When iron-filings are heated to redness in a porcelain tube, and vapor of water passed over them, the water undergoes decomposition with the utmost facility, hydrogen is rapidly disengaged, and the iron converted into oxide. On the other hand, oxide of iron heated in a tube through which a stream of dry hydrogen is passed, suffers almost instantaneous reduction to the metallic state, while the vapor of water, carried forward by the current of gas, escapes as a jet of steam from the extremity of the tube. In these experiments the affinities between the iron and oxygen and the hydrogen and oxygen are so nearly balanced, that the difference of *atmosphere* is sufficient to settle the point. An atmosphere of steam offers little resistance to the escape of hydrogen; one of hydrogen bears the same relation to steam; and this apparently trifling difference of circumstances is quite enough for the purpose.

The subject of chemical affinity is one of great interest, but too abstract and speculative to be discussed in detail in the present work.*

What is called the *nascent* state is one very favorable to chemical combination. Thus carbon and nitrogen refuse to combine with gaseous hydrogen; yet when these substances are simultaneously liberated from some

* See Mr. Graham's Elements, and Mr. Daniell's Introduction to Chemical Philosophy.

previous combination, they unite with great ease, as when organic matters are destroyed by heat, or by spontaneous putrefactive change. There is a strange and extraordinary, and at the same time very extensive class of actions, grouped together under the general title of cases of *disposing* affinity. The preparation of hydrogen from zinc and sulphuric acid is one of the most familiar. A piece of polished zinc or iron, put into pure water, manifests no power of decomposing the latter to the smallest extent; it remains perfectly bright for any length of time. On the addition, however, of a little sulphuric acid, hydrogen is at once freely disengaged, and the metal becomes oxidized and dissolved. Now the only intelligible function of the acid is to dissolve off the oxide as fast as it is produced; but why is the oxide produced when acid is present, and not otherwise? the question is very difficult to answer.

Great numbers of examples of this curious indirect action might be adduced. Metallic silver does not oxidize at any temperature; nay more, its oxide is easily decomposed by simple heat; yet if the finely-divided metal be mixed with siliceous matter and alkali, and ignited, the whole fuses to a yellow transparent glass of silicate of silver. Platinum is attacked by fused hydrate of potash; hydrogen is probably disengaged while the metal is oxidized; this is an effect which never happens to silver under the same circumstances, although silver is a much more oxidable substance than platinum. The fact is, that potash forms with the oxide of the last named metal a kind of saline combination, in which the oxide of platinum acts as an acid; and hence its formation under the *disposing* influence of the powerful base.

In the remarkable decompositions suffered by various organic bodies when heated in contact with caustic alkali or lime, we have other examples of the same fact. Products are generated which are never formed in the absence of the base; the reaction is invariably less complicated, and its results fewer in number and more definite, than in the event of simple destruction by a graduated heat. The preparation of light carburetted hydrogen by the new artificial process, already described, is an excellent example.

There is yet a still more obscure class of phenomena, in which effects are brought about by the mere *presence* of a substance, which itself undergoes no change whatever; the experiment mentioned in the article on oxygen, in which that gas is obtained, with the greatest facility, by heating a mixture of chlorate of potash and peroxide of manganese, is an excellent case in point. The salt is decomposed at a very far lower temperature than would otherwise be required. The oxide of manganese, however, is not in the slightest degree altered; it is found, after the experiment, in the same state as before. The name *katalysis* is sometimes given to these peculiar actions of contact; the expression is not significant, and may be for that reason the more admissible, as it suggests no explanation.

It is proper to remark, that the contact-decompositions alluded to are sometimes mixed up with other effects, which are, in reality, much more intelligible, as the action of finely-divided platinum upon certain gaseous mixtures, in which the solid really seems to have the power of condensing the gas upon its greatly extended surface, and thereby inducing combination by bringing the particles within the sphere of their mutual attractions.

ELECTRO-CHEMICAL DECOMPOSITION; CHEMISTRY OF THE VOLTAIC PILE.

When a voltaic current of considerable power is made to traverse various compound liquids, a separation of the elements of these liquids ensues; provided that the liquid be capable of conducting a current of a certain degree of energy, its decomposition almost always follows.

The elements are disengaged solely at the limiting surfaces of the liquid;

where, according to the common mode of speech, the current enters and leaves the latter, all the intermediate portions being perfectly quiescent. In addition, the elements are not separated indifferently and at random at these two surfaces, but, on the contrary, make their appearance with perfect uniformity and constancy at one or the other, according to their chemical character, namely oxygen, chlorine, iodine, acids, &c., at the surface connected with the *copper* or *positive* end of the battery; hydrogen, the metals, &c., at the surface in connection with the *zinc* or *negative* extremity of the arrangement.

The terminations of the battery itself, usually, but by no means necessarily, of metal, are designated as poles or *electrodes*,* as by their intervention the liquid to be experimented on is made a part of the circuit. The process of decomposition by the current is called *electrolysis*,† and the liquids, which when thus treated yield up their elements, are denominated *electrolytes*.

When a pair of platinum plates are plunged into a glass of water to which a few drops of oil of vitriol have been added, and the plates connected by wires with the extremities of an active battery, oxygen is disengaged at the positive electrode, and hydrogen at the negative, in the proportions of one measure of the former to two of the latter nearly. This experiment has before been described.‡

A solution of hydrochloric acid mixed with a little Saxon blue (indigo) and treated in the same manner, yields hydrogen on the negative side, and chlorine on the positive, the indigo there becoming bleached.

Iodide of potassium dissolved in water is decomposed in a similar manner, and with still greater ease; the free iodine at the positive side can be recognised by its brown color, or by the addition of a little gelatinous starch.

Every liquid is not an electrolyte; many refuse to conduct, and no decomposition can then occur; alcohol, ether, numerous essential oils, and other products of organic chemistry, besides a few saline inorganic compounds, act in this manner, and completely arrest the current of a very powerful battery. It is a very curious fact, and well deserves attention, that very nearly, if not all the substances acknowledged to be susceptible of electrolytic decomposition, belong to one class; they are all binary compounds, containing single equivalents of their components, the latter being strongly opposed to each other in their chemical relations, and held together by very powerful affinities.

The amount of power required to effect decompositions varies greatly; solution of iodide of potassium, melted chloride of lead, solution of hydrochloric acid, water mixed with a little oil of vitriol, and pure water, demand in this respect very different degrees of electrical force, the resistance to decomposition increasing from the first-mentioned substance to the last.

One of the most important and indispensable conditions of electrolysis is fluidity; bodies which, when reduced to the liquid condition, freely conduct and as freely suffer decomposition, become absolute insulators to the electricity of the battery when they become solid. Chloride of lead offers a good illustration of this fact; when fused in a little porcelain crucible it gives up its elements with the utmost ease, and a galvanometer, interposed somewhere in the circuit, is strongly affected. But when the source of heat is withdrawn, and the salt suffered to solidify, all signs of decomposition cease, and at the same moment the magnetic needle re-assumes its natural position. In the same manner the thinnest film of ice completely arrests the current of a powerful voltaic apparatus; the instant the ice is liquefied at any one point, so that water-communication may be restored between the electrodes, the current again passes, and decomposition occurs. Fusion by heat, and solution in aqueous liquids, answer the purpose equally well. A fluid substance may

* From ἤλεκτρον, and ὁδός, a way. † From ἤλεκτρον, and λύω, I loose. ‡ Page 98.

conduct a strong current of electricity without being decomposed; there are a few examples already known; however, no experiment has yet been recorded in which a solid was seen to undergo direct and unequivocal electrolysis.

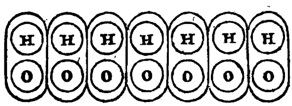
Liquids often exhibit the property of conduction for currents strong enough to be indicated by the galvanometer, but yet incapable of causing decomposition in the manner described. These currents may be conveyed through extensive masses of liquids; the latter seem, under these circumstances, to conduct after the manner of metals, without perceptible molecular change.

The metallic terminations of the battery, the poles or electrodes, have, in themselves, nothing in the shape of attractive or repulsive power for the elements so often separated at their surfaces. Finely-divided metal suspended in water, or chlorine held in solution in that liquid, shows not the least symptom of a tendency to accumulate around them; a single element is altogether unaffected, directly at least; severance from previous combination is required, in order that this appearance should be exhibited.

It is necessary to examine the process of electrolysis a little more closely. When a portion of water, for example, is subjected to decomposition in a glass vessel with parallel sides, oxygen is disengaged at the positive electrode, and hydrogen at the negative; the gases are perfectly pure and unmixed. If, while the decomposition is rapidly proceeding, the intervening water be examined by a beam of light, or by other means, not the slightest disturbance or movement of any kind will be perceived, nothing like currents in the liquid, or bodily transfer of gas from one part to another can be detected, and yet two portions of water, separated perhaps by an interval of four or five inches, may be respectively evolving pure oxygen and pure hydrogen.

There is, it would seem, but one mode of explaining this and all similar cases of regular electrolytic decomposition; this is by assuming that *all* the particles of water between the electrodes, and by which the current is conveyed, simultaneously suffer decomposition, the hydrogen travelling in one direction, and the oxygen in the other. The neighboring elements thus brought into close proximity, unite and reproduce water, again destined to be decomposed by a repetition of the same change. In this manner each particle of hydrogen may be made to travel towards the left, by becoming successively united to each particle of oxygen between itself and the negative electrode; when it reaches the latter, finding no disengaged particle of oxygen for its reception, it is rejected as it were from the series, and thrown off in a separate state. The same thing happens to each particle of oxygen, which at the same time passes continually towards the right, by combining successively with each particle of hydrogen, that moment separated, with which it meets, until at length it arrives at the positive plate or wire, and is disengaged. A succession of particles of hydrogen are thus continually thrown off from the decom-

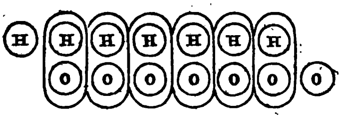
Fig. 117.



Water in usual state.

posing mass at one extremity, and a corresponding succession of particles of oxygen at the other. The power of the current is exerted with equal energy in every part of the liquid conductor, although its *effects* only become manifest at the very extremities. The action is one of a purely molecular or internal nature, and the metal terminations of the battery merely serve the purpose of

Fig. 118.



Water undergoing electrolysis.

completing the connection between the latter and the liquid to be decomposed. The figures 117 and 118 are intended to assist the imagination of the reader, who must at the same time avoid regarding them in any other light than that of a somewhat figurative mode of representing the curious phenomena described. The circles are intended to indicate the elements, and are distinguished by their respective symbols.

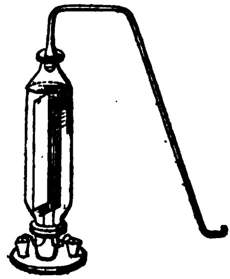
A distinction is to be carefully drawn between true and regular electrolysis, and what is called secondary decomposition, brought about by the reaction of the bodies so eliminated upon the surrounding fluid or upon the substance of the electrodes; hence the advantage of platinum for the latter purpose when electrolytic actions are to be studied in their greatest simplicity, that metal being scarcely attacked by any ordinary agents. When, for example, a solution of nitrate or acetate of lead is decomposed by the current between platinum plates, metallic lead is deposited at the negative side, and a brown powder, peroxide of lead, at the positive; the latter substance is the result of a secondary action; it proceeds, in fact, from the nascent oxygen, at the moment of its liberation, reacting upon the protoxide of lead present in the salt, and converting it into peroxide, which is insoluble in the dilute acid. There is every reason to believe that when sulphuric and nitric acids seem to be decomposed by the current, the effect is really due to the water they contain becoming decomposed, and reacting by its hydrogen upon the acid, for these bodies do not belong to the class of electrolytes, as already specified, and would probably refuse to conduct, could they be examined in an anhydrous condition.

It has generally been thought that the deposition of metal by the current must be considered as the consequence of a secondary action, as when a solution of sulphate of copper is electrolyzed, and copper reduced upon the surface of the negative electrode. This has been considered to arise from the water and sulphate of the oxide being simultaneously decomposed, and the subsequent action of the hydrogen upon the oxide of copper, by which the latter became reduced to the metallic state; but although this explanation has been rendered very doubtful by recent investigation, and a great number of cases of supposed secondary action thus referred to direct electrolysis, many indubitable examples of the phenomenon referred to yet remain.

If a number of different electrolytes, such as acidulated water, iodide of potassium, fused chloride of lead, &c., be arranged in a series, and the same current made to traverse the whole, all will suffer decomposition at the same time, but by no means to the same amount. If arrangements be made by which the quantities of the eliminated elements can be accurately ascertained, it will be found when the decomposition has proceeded to some extent, that these latter will have been disengaged exactly in the *ratio of the chemical equivalents.* The same current which decomposes 9 parts of water, will separate into their elements 165 parts of iodide of potassium, 139 parts of chloride of lead, &c. Hence the very important conclusion: The action of the current is perfectly definite in its nature, producing a fixed and constant amount of decomposition, expressed in each electrolyte by the value of its chemical equivalent.

From a very extended series of experiments, based on this and other methods of research, Mr. Faraday was enabled to draw the general inference, that effects of chemical decomposition were always proportionate to the quantity of circulating electricity, and might be taken as an accurate and trustworthy measure of the latter. Guided by this highly important principle, he constructed his *voltameter*, an instrument which has rendered the greatest service to electrical science. This is merely an arrangement by which a little acidulated water is decomposed by the current, the gas evolved being collected and measured. By placing such an instrument in any part of the circuit, the quantity of electric force necessary to produce any given effect can be at once estimated; or, on the other hand, any required amount of the latter can be, as it were, measured out and adjusted to the object in view. The voltameter has received many different forms; one of the most extensively useful is that figured, in which the platinum plates are separated by a very small interval, and the gas is collected in a graduated jar standing on the shelf of the pneumatic trough, the tube of the instrument, which is filled to the neck with dilute sulphuric acid, being passed beneath the jar.

Fig. 119.



The decompositions of the voltaic battery can be effected by the electricity of the common machine, by that developed by magnetic action, and by that of animal origin, but to an extent incomparably more minute. This arises from the very small *quantity* of electricity set in motion by the machine, although its *tension*, that is, power of overcoming obstacles and passing through imperfect conductors, is exceedingly great. A pair of small wires of zinc and platinum dipping into a single drop of dilute acid, develop far more electricity, to judge from the chemical effects of such an arrangement, than very many turns of a large plate electrical machine in high action. Nevertheless, polar or electrolytic decomposition can be distinctly and satisfactorily effected by the latter, although on a minute scale.

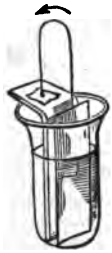
With a knowledge of the principles laid down, the study of the voltaic battery may be resumed and completed. In the first place, two very different views have been held concerning the source of the electrical disturbance in that apparatus. Volta himself ascribed it to mere contact of dissimilar metals; to what was denominated an *electro-motive* force, called into being by such contact; the liquid merely serving the purpose of a conductor between one pair of metals and that succeeding. Proof was supposed to be given of the fundamental position by an experiment in which discs of zinc and copper attached to insulating handles, after being brought into close contact, were found, by the aid of a very delicate gold-leaf electroscope, to be in opposite electrical states. It appears, however, that the more carefully this experiment is made, the smaller is the effect observed; and hence it is judged highly probable that the whole may be due to accidental causes, against which it is almost impossible to guard.

On the other hand, the observation was soon made that the power of the battery always bore some kind of proportion to the chemical action upon the zinc; that, for instance, when pure water was used, the effect was extremely feeble; with solution of salt, it became much greater; and lastly, with dilute acid, greatest of all; so that some relation evidently existed between the chemical effect upon the metal, and the evolution of electrical force.

The experiments of Mr. Faraday and Professor Daniell have given very

great support to the chemical theory, by showing that contact of dissimilar metals is *not* necessary in order to call into being powerful electrical currents, and that the development of electrical force is not only in some way connected with the chemical action of the liquid of the battery, but that it is always in direct proportion to the latter. One very beautiful experiment, in which decomposition of iodide of potassium by real electrolysis is performed by a current generated without any contact of dissimilar metals, can be thus made:—

Fig. 120.



A plate of zinc is bent at a right angle, and cleaned by rubbing with sand-paper. A plate of platinum has a wire of the same metal attached to it by careful riveting, and the latter bent into an arch. A piece of folded filter-paper is wetted with solution of iodide of potassium, and placed upon the zinc; the platinum plate is arranged opposite to the latter with the end of its wire resting upon the paper, and then the pair plunged into a glass of dilute sulphuric acid, mixed with a few drops of nitric. A brown spot of iodine becomes in a moment evident beneath the extremity of the platinum wire; that is, at the positive side of the arrangement.

A strong argument in favor of the chemical view is founded on the easily proved fact, that the direction of the current is determined by the kind of action upon the metals, the one least attacked being always positive. Let two polished plates, the one iron and the other copper, be connected by wires with a galvanometer, and then immersed in a solution of an alkaline sulphuret. The needle in a moment indicates a powerful current, passing from the copper, through the liquid, to the iron, and back again through the wire. Let the plates be now removed, cleaned, and plunged into dilute acid; the needle is again driven round, but in the opposite direction, the current now passing from the iron, through the liquid to the copper. In the first instance the copper is acted upon, and not the iron; in the second, these conditions are reversed, and with them, the direction of the current.

The metals employed in the practical construction of voltaic batteries are zinc for the active metal, and copper, silver, or, still better, platinum for the inactive one; the greater the difference of oxidability, the better the arrangement. The liquid is either dilute sulphuric acid, sometimes mixed with a little nitric, or occasionally, where very slow and long-continued action is wanted, salt and water. To obtain the maximum effect of the apparatus with the least expenditure of zinc, that metal must be employed in a pure state, or its surface must be covered by an amalgam of mercury, which in its electrical relations closely resembles the pure metal. The zinc is easily brought into this condition by wetting it with dilute sulphuric acid, and then rubbing a little mercury over it by means of a piece of rag tied to a stick.

The principle of the compound battery is, perhaps, best seen in the crown of cups; by each alternation of zinc, fluid, and copper, the current is urged forwards with increased energy, its intensity is augmented, but the actual amount of electrical force thrown into the current form is not increased. The quantity, estimated by its decomposing power, is in fact determined by that of the smallest and least active pair of plates, the quantity of electricity in every part or section of the circuit being exactly equal. Hence large and small plates, batteries strongly and weakly charged, can never be connected without great loss of power.

When a battery, either simple or compound, constructed with pure or with amalgamated zinc, is charged with dilute sulphuric acid, a number of highly interesting phenomena may be observed. While the circuit remains broken, the zinc is perfectly inactive, no water is decomposed, no hydrogen liberated;

but the moment the connection is completed, torrents of hydrogen arise, not from the zinc, but from the copper or platinum surfaces alone, while the zinc undergoes tranquil and imperceptible oxidation and solution. Thus, exactly the same effects are seen to occur in every active cell of a closed circuit, which are witnessed in a portion of water, undergoing electrolysis; the oxygen appears at the positive side, with respect to the current, and the hydrogen at the negative; but with this difference, that the oxygen, instead of being set free, combines with the zinc. It is, in fact, a real case of electrolysis, and electrolytes alone are available as exciting liquids.

Common zinc is very readily attacked and dissolved by dilute sulphuric acid; and this is usually supposed to arise from the formation of a multitude of little voltaic circles, by the aid of particles of foreign metals or plumbago, partially imbedded in the zinc. This gives rise in the battery to what is called local action, by which in the common forms of apparatus three-fourths or more of the metal is often consumed, without contributing in the least to the general effect, but, on the contrary, injuring the latter to some extent. This evil is got rid of by amalgamating the surface.

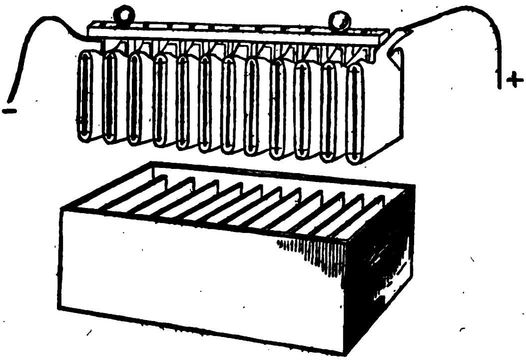
From experiments very carefully made with a "dissected" battery of peculiar construction, in which local action was completely avoided, it has been distinctly proved that the quantity of electricity set in motion by the battery varies exactly with the zinc dissolved. Coupling this fact with that of the definite action of the current, it will be seen, that when a perfect battery of this kind is employed to decompose water, in order to evolve 1 grain of hydrogen from the latter, 33 grains of zinc must be oxidized and its equivalent quantity of hydrogen disengaged in each active cell of the battery. That is to say, that the electrical force generated by the oxidation of an equivalent of zinc *in* the battery, is capable of effecting the decomposition of an equivalent of water, or any other electrolyte, *out* of it.

This is an exceedingly important discovery; it serves to show, in the most striking manner, the intimate nature of the connection between chemical and electrical forces, and their remarkable quantitative or equivalent relations. It almost seems, to use an expression of Mr. Faraday, as if a transfer of chemical force took place through the substance of solid metallic conductors; that chemical actions, called into play in one portion of the circuit, could be made at pleasure to exhibit their effects without loss or diminution in any other There is an hypothesis, not of recent date, long countenanced and supported by the illustrious Berzelius, which refers all chemical phenomena to electrical forces; which supposes that bodies combine because they are in opposite electrical states; even the heat and light accompanying chemical union may be, to a certain extent, accounted for in this manner. In short, we are in such a position, that either may be assumed as cause or effect; it may be that electricity is merely a form or modification of ordinary chemical affinity; or, on the other hand, that all chemical action is merely a manifestation of electrical force.

One of the most useful forms of the common voltaic battery is that contrived by Dr. Wollaston. The copper is made completely to encircle the zinc plate, except at the edges, the two metals being kept apart by pieces of cork or wood. Each zinc is soldered to the preceding copper, and the whole screwed to a bar of dry mahogany, so that the plates can be lifted into or out of the acid, which is contained in an earthenware trough, divided into separate cells. The liquid consists of a mixture of 100 parts water, 2½ parts oil of vitriol, and 2 parts commercial nitric acid, all by measure. A number of such batteries are easily connected together by straps of sheet copper, and admit of being put into action with great ease. (Fig. 121.)

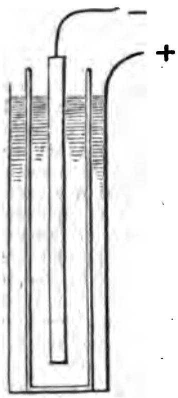
There are many serious evils felt even in this, the best of the old forms of voltaic apparatus; the local action is very great, and the diminution of pow-

Fig. 121.



extremely rapid, the effects of first immersion being sometimes ten times greater than those observed when the battery has been a little time in use. There are several causes which concur in producing this disagreeable result, such as the adhesion of hydrogen, in bubbles, to the surface of the copper; the precipitation of metallic zinc upon the latter, and others perhaps less obvious.

Fig. 122.

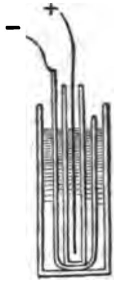


An instrument of immense value for purposes of electro-chemical research, in which it is desired to maintain powerful and equable currents for many successive hours, has been contrived by Professor Daniell. Each cell of this "constant" battery consists of a copper cylinder 3½ inches in diameter, and of a height varying from 6 to 18 inches. The zinc is employed in the form of a rod ¾ of an inch in diameter, carefully amalgamated, and suspended in the centre of the cylinder. A second cell of porous earthenware or animal membrane intervenes between the zinc and the copper; this is filled with a mixture of 1 part by measure of oil of vitriol and 8 of water, and the exterior space with the same liquid, saturated with sulphate of copper. A sort of little colander is fitted to the top of the cell, in which crystals of the sulphate of copper are placed, so that the strength of the solution may remain unimpaired. When a communication is made by a wire between the rod and the cylinder, a powerful current is produced, which may be exalted in intensity to almost any amount by connecting a sufficient number of such cells into a series, on the principle of the crown of cups; the copper of the first being attached to the zinc of the second. Ten such alternations constitute a very powerful apparatus, which has the great advantage of retaining its energy undiminished for a lengthened period. The interior of the cylinder becomes covered with a compact deposit of reduced copper; no gas is disengaged, and there is no local action on the zinc.

The battery of Professor Grove is another very beautiful combination, in which a principle of considerable importance is called prominently into play,

namely, the diminution of *resistance* to the passage of the current in the electrolyte by the affinity of one of the elements of the latter, or of some associated substance, for the liberated hydrogen.

Fig. 123.

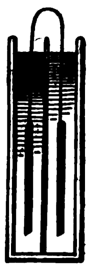


One of the cells of this battery is represented in the margin, in section. The zinc plate is bent round, so as to present a double surface, and well amalgamated; within it stands a thin flat cell of porous earthenware, filled with strong nitric acid, and the whole is immersed in a mixture of 1 part by measure of oil of vitriol and 6 of water, contained either in one of the cells of Wollaston's trough, or in a separate cell of glazed porcelain, made for the purpose. The apparatus is completed by a plate of platinum foil which dips into the nitric acid, and forms the positive side of the arrangement. With ten such pairs, experiments of decomposition, ignition of wires, the light between charcoal points, &c., can be exhibited with great brilliancy, while the battery itself is very compact and portable, and, to a great extent, constant in its action. The zinc, as in the case of Professor Daniell's battery, is only consumed while the current passes, so that the apparatus may be arranged an hour or two before it is required for use, which is often a matter of great convenience. The nitric acid suppresses the whole of the hydrogen, becoming thereby slowly de-oxidized and converted into nitrous acid, which at first remains dissolved, but after some time begins to be disengaged from the porous cells in dense red fumes; this constitutes the only serious drawback to this excellent instrument.

Mr. Smee has contrived an ingenious battery, in which silver covered with a thin coating of finely divided metallic platinum is employed in association with amalgamated zinc and dilute sulphuric acid. The rough surface appears to permit the ready disengagement of the bubbles of hydrogen.

Within the last three or four years several very beautiful and successful applications of voltaic electricity have been made, which may be slightly mentioned. Mr. Spencer and Professor Jacobi have employed it in copying, or rather in multiplying, engraved plates and medals, by depositing upon their surfaces a thick coating of metallic copper, which, when separated from the original, exhibits, in reverse, a most faithful representation of the latter By using this in its turn as a mould or matrix, an absolutely perfect *fac-simile* of the plate or medal is obtained. In the former case, the impressions taken on paper are quite undistinguishable from those directly derived from the work of the artist; and as there is no limit to the number of *electrotype* plates which can be thus produced, engravings of the most beautiful description may be multiplied indefinitely. The copper is very tough, and bears the action of the press perfectly well.

Fig. 124.

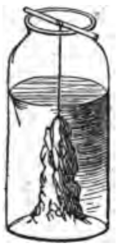


The apparatus used in this and many similar processes is of the simplest possible kind. A trough or cell of wood is divided by a porous diaphragm, made of a very thin piece of sycamore, into two parts; dilute sulphuric acid is put on one side, and a saturated solution of sulphate of copper, sometimes mixed with a little acid, on the other. A plate of zinc is soldered to a wire or strap of copper, the other end of which is secured by similar means to the engraved copper plate. The latter is then immersed in the solution of sulphate, and the zinc in the acid. To prevent deposition of copper on the back of the copper plate, that portion is covered with varnish. For medals and small works a porous earthenware cell, placed in a jelly-jar, may be used.

Other metals may be precipitated in the same manner, in a smooth and compact form, by the use of certain precautions which have been gathered by experience. Electro-gilding and plating are now carried on very largely and in great perfection by Messrs. Elkington. Even non-conducting bodies, as sealing-wax and plaster of Paris, may be coated with metal; it is only necessary, as Mr. Murray has shown, to rub over them the thinnest possible film of plumbago. Seals may thus be copied in a very few hours with unerring truth.

M. Becquerel, several years ago, published an exceedingly interesting account of certain experiments, in which crystallized metals, oxides, and other insoluble substances, had been produced by the slow and continuous action of feeble electrical currents, kept up for months, or even years. These products exactly resembled natural minerals, and, indeed, the experiments threw great light on the formation of the latter within the earth.*

Fig. 125.



The common but very pleasing experiment of the *lead tree* is greatly dependent on electro-chemical action. When a piece of zinc is suspended in a solution of acetate of lead, the first effect is the decomposition of a portion of the latter, and the deposition of metallic lead upon the surface of the zinc; it is simply a displacement of a metal by a more oxidable one. The change does not, however, stop here; metallic lead is still deposited in large and beautiful plates upon that first thrown down, until the solution becomes exhausted, or the zinc entirely disappears. The first portions of lead form, with the zinc, a voltaic arrangement of sufficient power to decompose the salt, under the peculiar circumstances in which the latter is placed, the metal is precipitated upon the negative portion, that is the lead, while the oxygen and acid are taken up by the zinc.

Professor Grove has contrived a battery in which an electrical current, of sufficient intensity to decompose water, is produced by the reaction of oxygen upon hydrogen. Each *element* of this interesting apparatus consists of a pair of glass tubes to contain the gases, dipping into a vessel of acidulated water. Both tubes contain platinum plates, covered with a rough deposit of finely-divided platinum, and furnished with conducting wires, which pass through the tops or sides of the tubes, and are hermetically sealed into the latter. When the tubes are charged with oxygen on the one side and hydrogen on the other, and the wires connected with a galvanoscope, the needle of the instrument becomes instantly affected; and when ten or more are combined in a series, the oxygen-tube of the one with the hydrogen-tube of the next, &c., while the terminal wires dip into acidulated water, a rapid stream of minute bubbles from either wire indicates the decomposition of the liquid; and when the experiment is made with a small voltameter, it is found that the oxygen and hydrogen disengaged exactly equal in amount the quantities absorbed by the act of combination in each tube of the battery.

* Traité de l'Electricité et du Magnétisme, iii. p. 239.

CHEMISTRY OF THE METALS.

THE metals constitute the second and larger group of elementary bodies. A great number of these are of very rare occurrence, being found only in a few scarce minerals; others are more abundant, and some few almost universally diffused throughout the whole globe. Some of these bodies are of most importance when in the metallic state; others, when in combination, chiefly as oxides, the metals themselves being almost unknown. Many are used in medicine and in the arts, and are essentially connected with the progress of civilization.

If arsenic and tellurium be included, the metals amount to forty-two in number.*

Physical properties.—One of the most remarkable and striking characters possessed by the metals is their peculiar lustre; this is so characteristic that the expression metallic lustre has passed into common speech. This property is no doubt connected with the extraordinary degree of opacity which the metals present in every instance. The thinnest leaves or plates, the edges of crystalline laminæ, arrest the passage of light in the most complete manner. An exception to this rule is usually made in favor of gold-leaf, which when held up to the day exhibits a greenish color, as if it were really endued with a certain degree of translucency; the metallic film is, however, always so imperfect that it becomes difficult to say whether the observed effect may not be in some measure due to multitudes of little holes, many of which are visible to the naked eye.

In point of color, the metals present a certain degree of uniformity; with three exceptions, viz., copper and titanium, which are red, and gold, which is yellow, all these bodies are included between the pure white of silver, and the bluish-gray tint of lead; bismuth, it is true, has a pinkish color, but it is very feeble.

The differences of specific gravity are very wide, passing from potassium and sodium, which are lighter than water, to platinum, which is nearly twenty-one times heavier than an equal bulk of that fluid.

* Three very imperfectly known new bodies, *didymium*, *erbium*, and *terbium*, discovered by Mosander, are not included in the list.

[To these may be added *pelopium* and *niobium*, discovered by Prof. H. Rose, *ruthenium* by Klaus, and *ilmenium*.—R. B.]

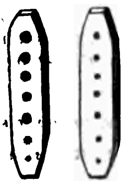
Table of the specific gravities of metals at 60° F.*

Platinum	20·98
Gold	19·26
Tungsten	17·60
Mercury	13·57
Palladium	11·30 to 11·8
Lead	11·35
Silver	10·47
Bismuth	9·82
Uranium	9·00
Copper	8·89
Cadmium	8·60
Cobalt	8·54
Arsenic	5·88
Nickel	8·28
Iron	7·79
Molybdenum	7·40
Tin	7·29
Zinc	6·86 to 7·1
Manganese	6·85
Antimony	6·70
Tellurium	6·11
Titanium	5·30
Sodium	·972
Potassium	·865

The property of malleability, or power of extension under the hammer, or between the rollers of the flatting-mill, is enjoyed by certain of the metals to a very great extent. Gold-leaf is a remarkable example of the tenuity to which a malleable metal may be brought by suitable means. The gilding on silver wire used in the manufacture of gold lace is even thinner, and yet presents an unbroken surface. Silver may be beaten out very thin; copper also, but to an inferior extent; tin and platinum are easily rolled out into foil; iron, palladium, lead, nickel, cadmium, the metals of the alkalies, and mercury, when solidified, are also malleable. Zinc may be placed midway between the malleable and brittle division; then perhaps bismuth, and lastly, such metals as antimony and arsenic, which are altogether destitute of malleability.

Ductility is a property distinct from the last, inasmuch as it involves the principle of tenacity, or power of resisting tension. The art of wire-drawing is one of great antiquity; it consists in drawing rods of metal through a succession of trumpet-shaped holes in a steel plate, each being a little smaller than its predecessor, until the requisite degree of fineness is attained. The metal often becomes very hard and rigid in this process, and is then liable to break; this is remedied by heating it to redness and suffering it to cool slowly, an operation which is termed annealing. The order of tenacity among the metals susceptible of being easily drawn into wire is the following: it is determined by observing the weights required to break asunder wires drawn through the same orifice of the plate.

Fig. 126.



* Dr. Turner, Elements, 446.

Iron	Gold
Copper	Zinc
Platinum	Tin
Silver	Lead

Metals differ as much in fusibility as in density; the following table, extracted from the late Dr. Turner's excellent work, will give an idea of their relations to heat. The melting-points of the metals which only fuse at a temperature above ignition, and that of zinc, are on the authority of Mr. Daniell, having been observed by the help of the pyrometer before described:—

		Melting points, Fahrenheit.
Fusible below a red heat.	Mercury	—39°
	Potassium	136°
	Sodium	190°
	Tin	442°
	Cadmium . . . . (about)	442°
	Bismuth	497°
	Lead	612°
	Tellurium—rather less fusible than lead.	
	Arsenic—unknown.	
	Zinc	773°
	Antimony—just below redness.	

		Melting points, Fahrenheit.
Infusible below a red heat.	Silver	1873°
	Copper	1996°
	Gold	2016°
	Cast-iron	2786°
	Pure iron, Nickel, Cobalt, Manganese, Palladium	Fusible only in an excellent wind-furnace.
	Molybdenum, Uranium, Tungsten, Chromium	Imperfectly melted in wind-furnace.
	Titanium, Cerium, Osmium, Iridium, Rhodium, Platinum, Columbium	Infusible in furnace; fusible by oxy-hydrogen blow-pipe.

Some metals acquire a pasty or adhesive state before becoming fluid; this is the case with iron and platinum, and also with the metals of the alkalies. It is this peculiarity which confers the very valuable property of welding, by which pieces of iron and steel are united without solder, and the finely-divided metallic sponge of platinum converted into a solid and compact bar.

Volatility is possessed by certain members of this class, and perhaps by all, could temperatures sufficiently elevated be obtained. Mercury boils and distils

below a red heat; potassium, sodium, zinc and cadmium rise in vapor when heated to bright redness; arsenic and tellurium are volatile.

Chemical relations.—Metallic combinations are of two kinds, namely, those formed by the union of metals among themselves, which are called alloys, or where mercury is concerned, amalgams, and those generated by combination with the non-metallic elements, as oxides, chlorides, sulphurets, &c. In this latter case the metallic characters are very frequently lost. The alloys themselves are really true chemical compounds, and not mere mixtures of the constituent metals; their properties often differ completely from those of the latter.

The oxides of the metals may be divided, as already pointed out, into three classes; namely, those which possess basic characters more or less marked, those which refuse to combine with either acids or alkalies, and those which have distinct acid properties. The strong bases are all protoxides; they contain single equivalents of metal and oxygen; the weaker bases are usually sesqui-oxides, containing metal and oxygen in the proportion of two equivalents of the former to three of the latter; the peroxides or neutral compounds are still richer in oxygen, and lastly, the metallic acids contain the maximum proportion of that element.

The gradual change of properties by increasing proportions of oxygen is well illustrated by the case of manganese.

	Metal.	Oxygen.	Symbols.	Characters.
Protoxide	1 eq.	1 eq.	MnO	Strongly basic.
Deutoxide	2 eq.	3 eq.	Mn_2O_3	Feebly basic.
Peroxide	1 eq.	2 eq.	MnO_2	Neutral.
Manganic acid	1 eq.	3 eq.	MnO_3	Strongly acid.
Hypermanganic acid	2 eq.	7 eq.	Mn_2O_7	Strongly acid.

The oxides of iron and chromium present similar, but less numerous gradations.

When a powerful oxygen-acid and a powerful metallic base are united in such proportions that they exactly destroy each other's properties, the resulting salt is said to be neutral; it is incapable of affecting vegetable colors. Now in all these well-characterized neutral salts, a constant and very remarkable relation is observed to exist between the quantity of *oxygen* in the base, and the quantity of *acid* in the salt. This relation is expressed in the following manner:—To form a neutral combination, as many equivalents of acid must be present in the salt as there are of oxygen in the base itself. In fact, this has become the very definition of neutrality, as the action on vegetable colors is sometimes an unsafe guide.

It is easy to see the application of this law. When a base is a protoxide, a single equivalent of acid suffices to neutralize it; when a sesquioxide, not less than three are required. Hence, if by any chance the base of a salt should pass by oxidation from the one state to the other, the acid will be insufficient in quantity by one-third to form a neutral combination. Protosulphate of iron offers an example; when a solution of this substance is exposed to the air it absorbs oxygen, and a yellow insoluble *sub-salt* is produced, which contains an excess of base. Four equivalents of the green compound absorb from the air two equivalents of oxygen, and give rise to one equivalent neutral, and one equivalent basic persulphate, as indicated by the diagonal zigzag line of division.

1 eq. iron + 1 eq. oxygen . . .	1 eq. sulphuric acid.	
1 eq. iron + 1 eq. oxygen . . .	1 eq. sulphuric acid.	
+ 1 eq. oxygen from air.		
1 eq. iron + 1 eq. oxygen . . .	1 eq. sulphuric acid.	
1 eq. iron + 1 eq. oxygen . . .	1 eq. sulphuric acid.	
+ 1 eq. oxygen from air.		

Such sub-salts are very frequently insoluble.

The combinations of chlorine, iodine, bromine, and fluorine with the metals, possess in a very high degree the saline character. If, however, the definition formerly given of a salt be rigidly adhered to, these bodies must be excluded from the class, and with them the very substance from which the name is derived, that is, common salt, which is a chloride of sodium. To obviate this anomaly it has been found necessary to create two classes of salts; in the first division will stand those constituted after the type of common salt, which contain a metal and a *salt-radical*, as chlorine, iodine, &c.; and in the second, those which, like sulphate of soda and nitrate of potash, are generally supposed to be combinations of an acid with an oxide. The names *haloid* salts*, and *oxygen acid*, or *oxy-salts*, are given to these two kinds.

When a haloid-salt is dissolved in water, it might be regarded as a combination of a metallic oxide with a hydrogen-acid, the water being supposed to undergo decomposition, its hydrogen being transferred to the salt radical, and its oxygen to the metal. This view is unsupported by evidence of any value; it is much more probable, indeed, that no truly saline compounds of hydrogen-acids exist, at any rate in inorganic chemistry. When a solution of any hydrogen acid is poured upon a metallic oxide, we may rather suppose that both are decomposed, water and a haloid-salt of the metal being produced. Take hydrochloric acid and potash by way of example.

Hydrochloric acid . .	Chlorine	Chloride potassium.
	Hydrogen	
Potash . .	Potassium	
	Oxygen	Water.

On evaporating the solution, the chloride of potassium crystallizes out.

When hydrochloric acid and ammoniacal gases are mixed, they combine with some energy and form a white solid salt, sal-ammoniac. Now this substance bears such a strong resemblance, in many important particulars, to chloride of potassium and common salt, that the ascription to it of a similar constitution is well warranted.

If chloride of potassium, therefore, contains chlorine and metal, sal-ammoniac may also contain chlorine in combination with a substance having the chemical relations of a metal, formed by the addition of the hydrogen of the acid to the elements of the ammonia.

Hydrochloric acid . .	1 eq. Chlorine	Chlorine	Sal-ammoniac.
	1 eq. Hydrogen		
Ammonia . .	3 eq. Hydrogen		
	1 eq. Nitrogen	Ammonium	

The term *ammonium* is given to this hypothetical body, NH_4; it is supposed to exist in all the ammoniacal salts. Thus we have chloride and iodide of ammonium, sulphate of the oxide of ammonia, &c. This view is very

* ἅλς, sea salt, and εἶδος, form.

strongly supported by the peculiarities of the salts themselves, as will hereafter be seen.

Many of the sulphurets also possess the saline character and are soluble in water, as those of potassium and sodium. Sometimes a pair of sulphurets will unite in definite proportions, and form a crystallizable compound. Such bodies bear a very close resemblance to oxygen-acid salts; they usually contain a mono-sulphuret of an alkaline metal, and a higher sulphuret of a non-metallic substance, or of a metal which has little tendency to form a basic oxide, the two sulphurets having exactly the same relation to each other as the oxide and acid of an ordinary salt. Hence the expressions *sulphur-salt*, *sulphur-acid*, and *sulphur-base*, which Berzelius applies to such compounds; they contain sulphur in the place of oxygen. Thus, bisulphuret of carbon is a sulphur-acid; it forms a crystallizable compound with simple sulphuret of potassium, which is a sulphur-base. Were oxygen substituted for the sulphur in this product, we should have carbonate of potash.

$$KS+CS_2 \text{ sulphur-salt.}$$
$$KO+CO_2 \text{ oxygen-salt.}$$

These remarkable compounds are very numerous and interesting; they have been studied by Berzelius with great care.

Salts often combine together and form what are called *double salts*, in which the same acid is in combination with two different bases. When sulphate of copper and sulphate of potash, or chloride of zinc and sal-ammoniac, are mixed in the ratio of the equivalents, dissolved in water, and the solution made to crystallize, double salts are obtained. These latter are often more beautiful, and crystallize better than their constituent salts.

Many of the compounds called *super*, or *acid salts*, such as bi-sulphate of potash, which have a sour taste and acid reaction to test paper, ought strictly to be considered in the light of double salts, in which one of the bases is water. Strange as it may at first sight appear, water possesses considerable basic powers, although it is unable to mask acid reaction on vegetable colors; hydrogen, in fact, very much resembles a metal in its chemical relations. Bisulphate of potash will therefore be a double sulphate of potash and water, while oil of vitriol must be assimilated to neutral sulphate of potash.

$$KO+SO_3 \text{ and } HO+SO_3$$

Water is a weak base; it is for the most part easily displaced by a metallic oxide; yet cases occur now and then in which the reverse happens, and water is seen to decompose a salt, in virtue of its basic power.

There are a few acid salts which contain no water; as the bichromate of potash, and a new anhydrous sulphate of potash discovered by M. Jacquelain.* It will be necessary of course to adopt some other view in these cases. The simplest will be to consider them as really containing two equivalents of acid to one of base.

By *water of crystallization* is meant water in a somewhat loose state of combination with a salt or other compound body, from which it can be disengaged by the mere application of heat, or by exposure to a dry atmosphere. Salts which contain water of crystallization have their crystalline form greatly influenced by the proportion of the latter. Green sulphate of iron crystallizes in two different forms, and with two different proportions of water, according to the temperature at which the salt separates from the solution.

* Ann. Chim. et Phys., lxx. p. 311.

Crystallization; Crystalline forms.—Almost every substance, simple and compound, capable of existing in the solid state, assumes, under favorable circumstances, a distinct geometrical form or figure, usually bounded by plane surfaces, and having angles of fixed and constant value. The faculty of crystallization seems to be denied only to a few bodies, chiefly highly complex organic principles, which stand as it were upon the very edge of organization, and which, when in a solid state, are frequently characterized by a kind of beady or globular appearance, well known to microscopical observers.

The most beautiful examples of crystallization are to be found among natural minerals, the result of exceedingly slow changes constantly occurring within the earth; it is invariably found that artificial crystals of salts and other soluble substances which have been slowly and quietly deposited, always surpass in size and regularity those of more rapid formation.

Solution in water or some other liquid is one very frequent method of effecting crystallization. If the substance be more soluble at a high than at a lower temperature, then a hot and saturated solution by slow cooling will generally be found to furnish crystals; this is a very common case with salts and various organic principles. If it be equally soluble, or nearly so, at all temperatures, then slow spontaneous evaporation in the air, or over a surface of oil of vitriol, often proves very effective.

Fusion and slow cooling may be employed in many cases; that of sulphur is a good example; the metals usually afford traces of crystalline figure when thus treated, which sometimes becomes very beautiful and distinct, as with bismuth. A third condition under which crystals very often form, is in passing from a gaseous to a solid state, of which iodine affords a good instance. When by any of these means time is allowed for the symmetrical arrangement of the particles of matter at the moment of solidification, crystals are produced.

That crystals owe their figure to a certain regularity of internal structure is shown both by their mode of formation and also by the peculiarities attending their fracture. A crystal placed in a slowly evaporating saturated solution of the same substance grows or increases by a continued deposition of fresh matter upon its sides in such a manner that the angles formed by the meeting of the latter remain unaltered.

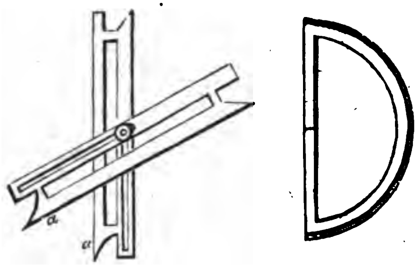
The tendency of most crystals to split in particular directions, called by mineralogists *cleavage*, is a certain indication of regular structure, while the curious optical properties of many among them, and their remarkable mode of expansion by heat, point to the same conclusion.

It may be laid down as a general rule that every substance has its own crystalline form, by which it may very frequently be recognized at once; not that each substance has a different figure, although very great diversity in this respect is to be found. Some forms are much more common than others, as the cube and six-sided prism, which are very frequently assumed by a number of bodies, not in any way related.

The same substance may have, under different sets of circumstances, as high and low temperatures, two different crystalline forms, in which case it is said to be *dimorphous*. Sulphur and carbon furnish, as already noticed, examples of this curious fact; another case is presented by carbonate of lime in the two modifications of calcareous spar and arragonite, both chemically the same, but physically different. A fourth example might be given in the iodide of mercury, which also has two distinct forms, and even two distinct colors, offering as great a contrast as those of diamond and plumbago.

The angles of crystals are measured by means of instruments called *goniometers*, of which there are two kinds in use, namely, the old or common goniometer, and the reflective goniometer of Dr. Wollaston.

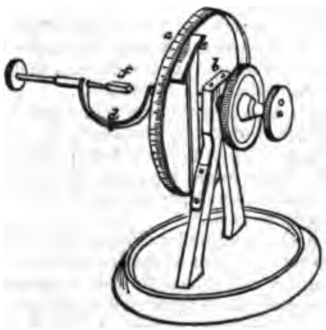
Fig. 127.



The common goniometer consists of a pair of steel blades moving with friction upon a centre, as shown in the cut. The edges *a a* are carefully adjusted to the faces of the crystal, whose inclination to each other it is required to ascertain, and then the instrument being applied to the divided semicircle, the contained angle is at once read off. An approximative measurement, within one or two degrees, can be easily obtained by this instrument, provided the planes of the crystal be tolerably perfect, and large enough for the purpose. Some practice is of course required before even this amount of accuracy can be attained.

The reflective goniometer is a very superior instrument, its indications being correct within a fraction of a degree; it is applicable also to the measurement of the angles of crystals of very small size, the only conditions required being that their planes be smooth and brilliant. The subjoined sketch will convey an idea of its nature and mode of use.

Fig. 128.

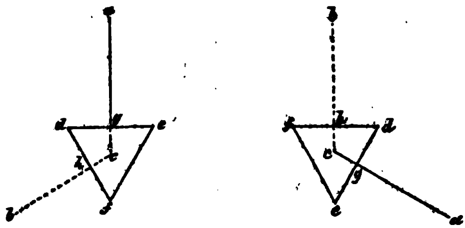


a is a divided circle or disc of brass, the axis of which passes stiffly and without shake through the support *b*. This axis is itself pierced to admit the passage of a round rod or wire, terminated by the milled-edged head *o*, and destined to carry the crystal to be measured by means of the jointed arm *d*. A vernier, *e*, immovably fixed to the upright support, serves to measure with great accuracy the angular motion of the divided circle. The crystal at *f* can

thus be turned round or adjusted in any desired position without the necessity of moving the disc.

The principle upon which the measurement of the angle rests is very simple. If the two adjacent planes of a crystal be successively brought into the same position, the angle through which the crystal will have moved will be *the supplement to that contained between the two planes.* This will be easily intelligible by reference to the subjoined diagram, in which a crystal having the form of a triangular prism* is shown in the two positions, the angle to be measured being that indicated by the letters *e d f*.

Fig. 129.



The lines *a c*, *b c* are perpendicular to the respective faces of the crystal, consequently the internal angles *d g c*, *d h c*, are right angles. Now, since the sum of the internal angles of a four-sided rectilineal figure, as *d g c h*, equal *four* right-angles, or 360°, the angle *g d h* (or *e d f*) must of necessity be the supplement to the angle *g c h*, or that through which the crystal moves. All that is required to be done, therefore, is to measure the latter angle with accuracy, and subtract its value from 180°; and this the goniometer effects.

One method of using the instrument is the following:—the goniometer is placed at a convenient height upon a steady table in front of a well-illuminated window. Horizontally across the latter, at the height of eight or nine feet from the ground, is stretched a narrow black riband, while a second similar riband, adjusted parallel to the first, is fixed beneath the window, a foot or eighteen inches above the floor. The object is to obtain two easily-visible black lines, perfectly parallel. The crystal to be examined is attached to the arm of the goniometer at *f* by a little wax, and adjusted in such a manner that the edge joining the two planes whose inclination is to be measured shall nearly coincide with, or be parallel to, the axis of the instrument. This being done, the adjustment is *completed* in the following manner:—the divided circle is turned until the zero of the vernier comes to 180°; the crystal is then moved round by means of the inner axis *c* (fig. 128) until the eye placed near it perceives the image of the upper black line reflected from the surface of one of the planes in question. Following this image, the crystal is still cautiously turned until the upper black line seen by reflection approaches and overlaps the lower black line seen *directly* by another portion of the pupil. It is obvious, that if the plane of the crystal be quite parallel to the axis of the instrument, (the latter being horizontal,) the two lines will coincide completely. If, however, this should not be the case, the crystal must be moved upon the wax until the two lines fall in one when superposed. The second face of the crystal must then be adjusted in the same manner, care being

* The triangular prism has been chosen for the sake of simplicity; but a moment's consideration will show that the rule applies equally well to any other figure.

taken not to derange the position of the first. When by repeated observation it is found that both have been correctly placed, so as to bring the edge into the required condition of parallelism with the axis of motion, the measurement of the angle may be made.

For this purpose the crystal is moved as before by the inner axis until the image of the upper line, reflected from the first face of the crystal, covers the lower line seen directly. The great circle, carrying the whole with it, is then cautiously turned until the same coincidence of the upper with the lower line is seen by means of the second face of the crystal; that is, the second face is brought into exactly the same position as that previously occupied by the first. Nothing then remains but to read off by the vernier the angle through which the circle has been moved in this operation. The division upon the circle itself is very often made *backwards*, so that the angle of motion is not obtained, but its supplement, or the angle of the crystal required.

It may be necessary to remark, that although the principle of the operation described is in the highest degree simple, its successful practice requires considerable skill and experience.

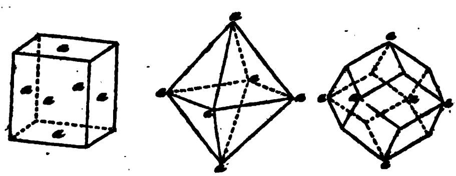
If a crystal of tolerably simple form be attentively considered it will become evident that certain directions can be pointed out in which straight lines may be imagined to be drawn, passing through the central point of the crystal from side to side, from end to end, or from one angle to that opposed to it, &c., about which lines the particles of matter composing the crystal may be conceived to be symmetrically built up. Such lines or *axes* are not always purely imaginary, however, as may be inferred from the remarkable optical properties of many crystals; upon their number, relative lengths, position and inclination to each other depends the outward figure of the crystal itself.

All crystalline forms may upon this plan be arranged in six classes or *systems*:—these are as follows:—

1. *The regular system.*—The crystals of this division have three equal axes, all placed at right angles to each other. The most important forms are the *cube* (1), the *regular octahedron* (2), and the *rhombic dodecahedron* (3).

Fig. 130.

1 2 3

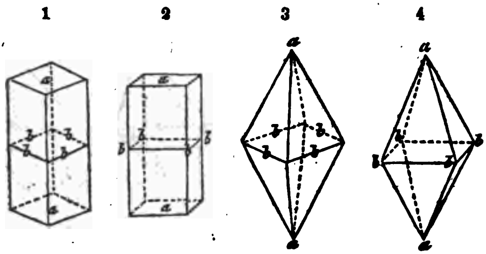


The letters *a—a* show the terminations of the three axes, placed as stated.

Very many substances, both simple and compound, assume these forms, as most of the metals, carbon in the state of diamond, common salt, iodide of potassium, the alums, fluor-spar, bisulphuret of iron, garnet, spinelle, &c.

2. *The square prismatic system.*—Three axes are here also observed, at right angles to each other. Of these, however, two only are of equal length, the third being usually longer or shorter. The most important forms are: A *right square prism*, in which the lateral axes terminate in the central point of each side (1); a *second* right square prism, in which the axes terminate in the edges (2); a corresponding pair of *right, square based octahedra* (3 and 4).

Fig. 131.

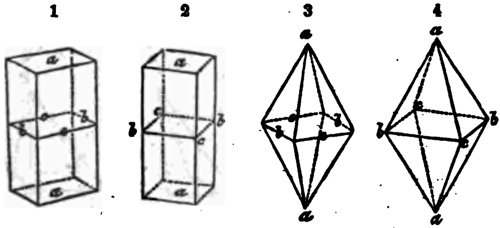


a—a. Principal, or vertical axis.
b—b. Secondary, or lateral axes.

Examples of these forms are to be found in zircon, native oxide of tin, apophyllite, yellow ferrocyanide of potassium, &c.

3. *The right prismatic system.*—This is characterized by three axes of unequal lengths, placed at right-angles to each other, as in the *right rectangular prism* (1), the right rhombic prism (2), the *right rectangular-based octahedron* (3), and the *right rhombic based octahedron* (4).

Fig. 132.

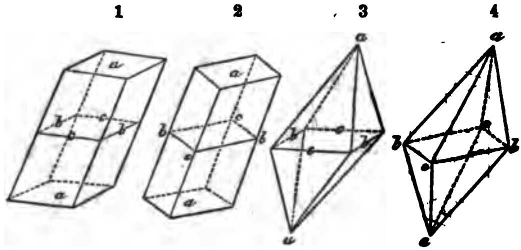


a—a. Principal axis.
b—b, *c—c*. Secondary axes.

The system is exemplified in sulphur crystallized at a low temperature, arsenical iron pyrites, nitrate and sulphate of potash, sulphate of baryta, &c.

4. *The oblique prismatic system.*—Crystals belonging to this group have also three axes, which may be all unequal; two of these (the secondary) are placed at right angles, the third being so inclined as to be oblique to one and perpendicular to the other. To this system may be referred the four following forms: *The oblique rectangular prism* (1), *the oblique rhombic prism* (2), *the oblique rectangular-based octahedron* (3), *the oblique rhombic-based octahedron* (4).

Fig. 133.

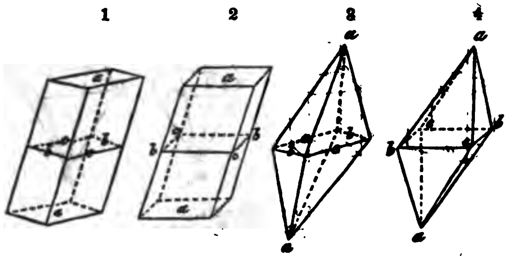


a—a. Principal axis.
b—b, c—c. Secondary axes.

Such forms are taken by sulphur crystallized by fusion and cooling, realgar, sulphate, carbonate, and phosphate of soda, borax, green vitriol, and many other salts.

5. *The doubly-oblique prismatic system.*—The crystalline forms comprehended in this division are, from their great apparent irregularity, exceedingly difficult to study and understand. In them are traced three axes, which may be all unequal in length, and are all oblique to each other, as in the two *doubly-oblique prisms* (1 and 2), and in the corresponding *doubly oblique octahedra* (3 and 4).

Fig. 134.

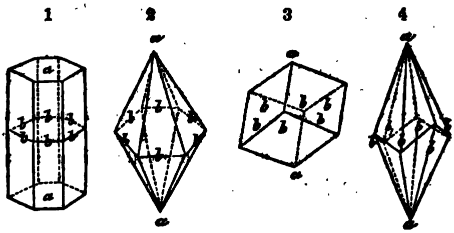


a—a. Principal axis, as before.
b—b, c—c. Secondary axes.

Sulphate of copper, nitrate of bismuth, and quadroxalate of potash, afford illustrations of these forms.

6. *The rhombohedral system.*—This is very important and extensive; it is characterized by the presence of *four* axes, three of which are equal, in the same plane, and inclined to each other at angles of 60°, while the fourth or principal axis is perpendicular to all. The *regular six-sided prism* (1), the *quartz-dodecahedron* (2), the *rhombohedron* (3), and a *second* dodecahedron, whose faces are scalene triangles (4), belong to the system in question.

Fig. 135.

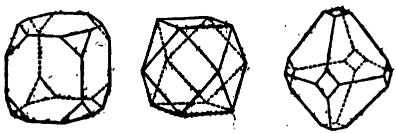


a—a. Principal axis.
b—b. Secondary axes.

Examples are readily found; as in ice, calcareous spar, nitrate of soda, beryl, quartz or rock crystal, and the semi-metals, arsenic, antimony and tellurium.

If a crystal increase in magnitude by equal additions on every part, it is quite clear that its figure must remain unaltered; but, if from some cause this increase should be partial, the newly-deposited matter being distributed unequally, but still in obedience to certain definite laws, then alterations of form are produced, giving rise to figures which have a direct geometrical connection with that from which they are derived. If, for example, in the cube, a regular omission of successive rows of particles of matter in a certain order be made at each solid angle, while the crystal continues to increase elsewhere, the result will be the production of small triangular planes, which as the process advances, gradually usurp the whole of the surface of the crystal, and convert the cube into an octahedron. The new planes are called *secondary*, and their production is said to take place by regular *decrements* upon the solid angles. The same thing may happen on the edges of the cube; a new figure, the rhombic dodecahedron, is then generated. The modifications which can thus be produced of the original or *primary* figure;—all of which are subject to exact geometrical laws;—are very numerous. Several distinct modifications may be present at the same time, and thus render the form exceedingly complex.

Fig. 136.



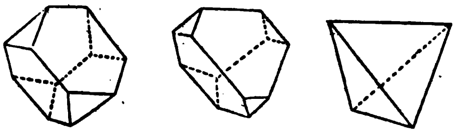
Passage of cube to octahedron.

It is important to observe, that in all these deviations from what may be regarded as the primary or fundamental figure of the crystal, the modifying planes are in fact *the planes of figures belonging to the same natural group or crystallographical system as the primary form, and having their axes coincident with those of the latter*. The crystals of each system are thus subject to a peculiar and distinct set of modifications, the observation of which very frequently constitutes an excellent guide to the discovery of the primary form itself.

Crystals often cleave parallel to all the planes of the primary figure, as in calcareous spar, which offers a good illustration of this perfect cleavage. Sometimes one or two of these planes have a kind of preference over the rest in this respect, the crystal splitting readily in these directions only.

A very curious modification of the figure sometimes occurs by the excessive growth of each alternate plane of the crystal; the rest become at length obliterated, and the crystal assumes the character called *hemihedral* or *half-sided.* This is well seen in the production of the tetrahedron from the regular octahedron, and of the rhombohedric form by a similar change from the quartz-dodecahedron already figured.

Fig. 137.



Passage of octahedron to tetrahedron.

Relations of form and constitution; isomorphism.—Certain substances to which a similar chemical constitution is ascribed, possess the remarkable property of exactly replacing each other in crystallized compounds without alteration of the characteristic geometrical figure. Such bodies are said to be *isomorphous.**

For example, magnesia, oxide of zinc, oxide of copper, protoxide of iron, and oxide of nickel, are allied by isomorphic relations of the most intimate nature. The salts formed by these substances with the same acid and similar proportions of water of crystallization, are identical in their form, and when of the same color, cannot be distinguished by the eye; the sulphates of magnesia and zinc may be thus confounded. The sulphates too all combine with sulphate of potash and sulphate of ammonia, giving rise to double salts, whose figure is the same, but quite different from that of the simple sulphates. Indeed this connection between identity of form and parallelism of constitution runs through all their combinations.

In the same manner alumina and peroxide of iron replace each other continually without change of crystalline figure; the same remark may be made of potash, soda, and ammonia with an equivalent of water, or oxide of ammonium, these bodies being strictly isomorphous. The alumina in common alum may be replaced by peroxide of iron; the potash by ammonia, or by soda, and still the figure of the crystal remains unchanged.

When compounds are thus found to correspond, it is inferred that the elements composing them are also isomorphous. Thus the metals magnesium, zinc, iron, and copper are presumed to be isomorphous; arsenic and phosphorus should present the same crystalline form, because arsenic and phosphoric acids give rise to combinations which agree most completely in figure and constitution. The chlorides, iodides, bromides, and fluorides agree, whenever they can be observed, in the most perfect manner; hence the elements themselves are believed to be also isomorphous. Unfortunately, for obvious reasons, it is very difficult to observe the crystalline figure of most of the elementary bodies.

Anomalies in the composition of various earthy minerals which formerly

* From ἴσος, equal, and μορφὴ, shape, or form.

threw much obscurity upon their chemical nature, have been in great measure explained by these discoveries.

Specimens of the same mineral from different localities were found to afford very discordant results on analysis. But the proof once given of the extent to which substitution of isomorphous bodies may go without destruction of what may be called the primitive type of the compound, these difficulties vanish.

Another benefit conferred on science by the discoveries in question, is that of furnishing a really philosophical method of classifying elementary and compound substances, so as to exhibit their natural relationships; it would be perhaps more proper to say that such will be the case when the isomorphic relations of all the elementary bodies become known,—at present only a certain number have been traced.

Decision of a doubtful point concerning the constitution of a compound may now and then be very satisfactorily made by a reference to this same law of isomorphism. Thus, alumina, the only known oxide of aluminum, is judged to be a sesquioxide of the metal from its relation to peroxide of iron, which is certainly so; the black oxide of copper is inferred to be really the protoxide, although it contains twice as much oxygen as the red oxide, because it is isomorphous with magnesia and zinc, both undoubted protoxides.

The subjoined table will serve to convey some idea of the most important families of isomorphous elements; it is taken from Professor Graham's systematic work, to which the pupil is referred for fuller details on this interesting subject.

Isomorphous groups.

(1.)	(3.)	(6.)
Chlorine	Phosphorus	Magnesium
Iodine	Arsenic	Manganese
Bromine	Antimony.	Iron
Fluorine.	(4.)	Cobalt
(2.)	Barium	Nickel
Sulphur	Strontium	Zinc
Selenium	Lead.	Copper
Tellurium.	(5.)	Cadmium
	Silver	Aluminum
	Sodium	Chromium
	Potassium	Calcium
	Ammonium.	Hydrogen ?

There is a law concerning the formation of double salts which may now be mentioned; the two bases are never taken from the same isomorphous family. Sulphate of copper or of zinc may unite in this manner with sulphate of soda or potash, but not with sulphate of iron or cobalt; chloride of magnesium may combine with chloride of ammonium, but not with chloride of zinc or nickel, &c. It will be seen hereafter that this is a matter of some importance in the theory of the organic acids.

Polybasic acids.—There is a particular class of acids in which a departure occurs from the law of neutrality formerly described; these are acids requiring two or more equivalents of a base for neutralization. The phosphoric and arsenic acids present the only examples yet known in mineral chemistry, but in the organic department of the science cases very frequently occur.

Phosphoric acid is capable of existing in three different states or modifications, forming three separate classes of salts which differ completely in properties and constitution. They are distinguished by the names *tribasic*, *bibasic*,

and *monobasic* acids, according to the number of equivalents of base required to form neutral salts.

Tribasic, or *common phosphoric acid.*—When commercial phosphate of soda is dissolved in water and the solution mixed with acetate of lead, an abundant white precipitate of phosphate of lead falls, which may be collected on a filter, and well washed. While still moist, this compound is suspended in distilled water, and an excess of sulphuretted hydrogen gas passed. The oxide of lead is converted into sulphuret, which subsides as a black insoluble precipitate, while phosphoric acid remains in solution, and is easily deprived of the residual sulphuretted hydrogen by gentle heat.

The soda-salt employed in this experiment contains the tribasic modification of phosphoric acid; of the three equivalents of base, two consist of soda and one of water; when mixed with solution of lead, a tribasic phosphate of the oxide of that metal falls, which, when decomposed by sulphuretted hydrogen, yields sulphuret of lead and a hydrate of the acid containing three equivalents of water in intimate combination.

Phosphate of soda	2 eq. soda	2 eq. acetate of soda.
	1 " water	1 " hydrated acetic acid.
	1 " phosphoric acid	
3 eq. acetate of lead	2 eq. acetic acid	
	1 " acetic acid	
	3 " oxide of lead	1 eq. tribasic phosphate of lead.

1 eq. tribasic phosphate of lead	3 eq. lead	3 eq. sulphuret of lead.
	3 " oxygen	
	1 " phosphoric acid	
3 eq. sulphuretted hydrogen	3 eq. sulphur	
	3 " hydrogen	1 eq. tribasic hydrate of phosphoric acid.

The solution of tribasic hydrate may be concentrated by evaporation in vacuo over sulphuric acid until it crystallizes in thin deliquescent plates. The same compound in beautiful crystals, resembling those of sugar-candy, has been accidentally formed.* It undergoes no change by boiling with water, but when heated alone to 400° loses some of its combined water and becomes converted into a mixture of the bibasic and monobasic hydrates. At a red-heat, it becomes entirely changed to monohydrate, which, at a still higher temperature, sublimes.

Tribasic phosphoric acid is characterized by the yellow insoluble salt it forms with oxide of silver.

Bibasic phosphoric acid; otherwise called pyrophosphoric acid.—When common phosphate of soda, containing

$$2NaO, HO, PO_5 + 24HO$$

is gently heated, the 24 equivalents of water of crystallization are expelled, and the salt becomes anhydrous, but if the heat be raised to a higher point, the basic water is also driven off, and the acid passes into the second or bibasic modification. If the altered salt be now dissolved in water, this new compound, the bibasic phosphate of soda, crystallizes out. When mixed with solution of acetate of lead, bibasic phosphate of lead is thrown down,

* Péligot, Ann. Chim. et Phys., lxxiii. p. 266.

which, decomposed by sulphuretted hydrogen, furnishes a solution of the bibasic hydrate. This solution may be preserved without change at common temperatures, but when heated, an equivalent of water is taken up, and the substance passes back again into the tribasic modification.

Crystals of this hydrate have also been observed by M. Peligot. Their production was also accidental. The bibasic phosphates soluble in water give a white precipitate with solution of silver.

Monobasic, or metaphosphoric acid.—When common tribasic phosphate of soda is mixed with solution of tribasic hydrate of phosphoric acid, and exposed after proper concentration to a low temperature, prismatic crystals are obtained, which consist of a phosphate of soda having two equivalents of basic water.

$$NaO, 2HO, PO_5+2HO.$$

When this salt is very strongly heated, both the water of crystallisation and that contained in the base are expelled, and monobasic phosphate of soda remains. This may be dissolved in cold water, precipitated with acetate of lead, and the lead-salt as before decomposed by sulphuretted hydrogen.

The solution of the monobasic hydrate is decomposed rapidly by heat, becoming converted into tribasic hydrate. It possesses the property of coagulating albumen, which is not enjoyed by either of the preceding modifications. Monobasic alkaline phosphates precipitate nitrate of silver white.

The glacial phosphoric acid of pharmacy is, when pure, hydrate of monobasic phosphoric acid; it contains HO, PO_5.

Anhydrous phosphoric acid, prepared by burning phosphorus in dry air, when thrown into water forms a variable mixture of the three hydrates. When heated, a solution of the tribasic hydrate alone remains.*

Binary theory of salts.—The great resemblance in properties between the two classes of saline compounds, the haloid and oxy-salts, has very naturally led to the supposition that both might possibly be alike constituted, and that the latter, instead of being considered compounds of an oxide and an acid, might with greater propriety be considered to contain a metal in union with a compound salt-radical, having the chemical relation of chlorine and iodine. On this supposition sulphate and nitrate of potash will be constituted in the same manner as chloride of potassium, the compound radical replacing the simple one.

Old view.	New view.
$KO+SO_3$	$K+SO_4$
$KO+NO_5$	$K+NO_6$

Hydrated sulphuric acid will be like hydrochloric acid, a hydruret of a salt-radical.

$$H+SO_4.$$

When the latter acts upon metallic zinc, the hydrogen is simply displaced, and the metal substituted; no decomposition of water is supposed to occur, and, consequently, the difficulty of the old hypothesis is at an end. When the acid is poured upon a metallic oxide, the same reaction occurs as in the case of hydrochloric acid, water and a haloid-salt are produced. All acids must

* The three modifications of phosphoric acid possess properties so dissimilar that they might really be considered three distinct, although intimately related, bodies. It is exceedingly remarkable that when their salts are subjected to electro-chemical decomposition, the *acids travel unaltered*, a tribasic salt giving at the positive electrode a solution of common phosphoric acid, a bibasic salt, one of pyrophosphoric acid, and a monobasic salt, one of metaphosphoric acid. (Professor Daniell and Dr. Miller, Phil. Trans. for 1844, p. 1.)

be, in fact, hydrogen acids, and all salts haloid-salts, with either simple or compound radicals.

This simple and beautiful theory is not by any means new; it was suggested by Davy, who proposed to consider hydrogen as the acidifying principle in the common acids. It is supported by a good deal of evidence derived from various sources, and has lately received great help from a series of exceedingly interesting experiments on the electrolysis of saline solutions, by Professor Daniell.* The necessity of creating a great number of non-isolable compounds is often urged as an objection to the new view; but the same objection applies to the old mode of considering the subject; a compound of 1 eq. nitrogen, and 5 eq. oxygen is as hypothetical as one containing 6 eq. of oxygen. Absolute nitric acid is altogether unknown; the same remark applies to almost every one of the organic acids; and, what is well worthy of notice, those acids which, like sulphuric, phosphoric, and carbonic acids, may be obtained in a separate state, are *destitute of all acid properties so long as the anhydrous condition is retained.*

The real difficulty in the general application of the binary theory is presented by the three modifications of phosphoric acid. If this could be explained away in a satisfactory manner, there seems no reason to object to its adoption, which would greatly simplify many parts of the science. One great inconvenience would be the change of nomenclature involved.

CLASSIFICATION OF METALS.

1.

Metals of the Alkalis.

Potassium,	Lithium,
Sodium,	Ammonium.†

2.

Metals of the Alkaline Earths.

Barium,	Calcium,
Strontium,	Magnesium.

3.

Metals of the Earths Proper.

Aluminum,	Zirconium,
Glucinium,	Thorium.
Yttrium,	

4.

Oxidable Metals Proper, whose Oxides form powerful Bases.

Manganese,	Cadmium,
Iron,	Bismuth,
Nickel,	Lead,
Cobalt,	Uranium,
Copper,	Cerium,
Zinc,	Lantanum.

* See Daniell's Introduction to Chemical Philosophy, 2d. edit., p. 533.

† This hypothetical substance is merely placed with the metals for the sake of convenience, as will be apparent in the sequel.

5.

Oxidable Metals Proper, whose Oxides form weak Bases, or Acids.

Chromium,
Vanadium,
Tungsten,
Molybdenum,
Columbium,
Titanium,
Tin,
Antimony,
Arsenic,
Tellurium,
Osmium.

6.

Metals Proper, whose Oxides are reduced by Heat; Noble Metals.

Gold,
Mercury,
Silver,
Platinum,
Palladium,
Iridium,
Rhodium.

SECTION I.

METALS OF THE ALKALIS.

POTASSIUM.

Potassium was discovered by Sir H. Davy in 1807, who obtained it in very small quantity by exposing a piece of moistened hydrate of potash to the action of a powerful voltaic battery, the alkali being placed between a pair of platinum plates put into connection with the apparatus. Processes have since been devised for obtaining this curious metal in almost any quantity that can be desired.

An intimate mixture of carbonate of potash and charcoal is prepared by calcining, in a covered iron pot, the crude tartar of commerce; when cold, it is rubbed to powder, mixed with one-tenth part of charcoal in small lumps, and quickly transferred to a retort of stout hammered iron; the latter may be one of the iron bottles in which mercury is imported, a short and somewhat wide iron tube having been fitted to the aperture. The retort is placed upon its side, in a furnace so constructed that the flame of a very strong fire, fed with dry wood, may wrap round it, and maintain every part at a uniform degree of heat, approaching to whiteness. A copper receiver, divided in the centre by a diaphragm, is connected to the iron pipe, and kept cool by the application of ice, while the receiver itself is partly filled with naphtha or rock-oil, in which the potassium is to be preserved. Arrangements being thus completed, the fire is gradually raised until the requisite temperature is reached, when decomposition of the alkali by the charcoal commences, carbonic oxide gas is abundantly disengaged, and potassium distils over, and falls in large melted drops into the liquid. The pieces of charcoal are introduced for the purpose of absorbing the melted carbonate of potash, and preventing its separation from the finely-divided carbonaceous matter.

If the potassium be wanted absolutely pure, it must be afterwards redistilled in an iron retort, into which some naphtha has been put, that its vapor may expel the air, and prevent oxidation of the metal.

Potassium is a brilliant white metal, with a high degree of lustre; at the common temperature of the air it is soft, and may be easily cut with a knife, but at 32° it is brittle and crystalline. It melts completely at 150°, and distils at a low red-heat. The density of this remarkable metal is only ·865, water being unity.

Exposed to the air, potassium oxidizes instantly, a tarnish covering the surface of the metal, which quickly thickens to a crust of caustic potash. Thrown upon water, it takes fire spontaneously, and burns with a beautiful purple flame, yielding an alkaline solution. When brought into contact with a little water in a jar standing over mercury, the liquid is decomposed with great energy, and hydrogen liberated. Potassium is always preserved under the surface of naphtha.

The equivalent of potassium (kalium) is 39·19, and its symbol K.

There are two compounds of this metal with oxygen,—potash and peroxide of potassium.

Potash or protoxide, KO, is produced when potassium is heated in dry air; the metal burns, and becomes entirely converted into a volatile, fusible, white substance, which is anhydrous potash. Moistened with water, it evolves great heat, and forms the hydrate.

Hydrate of potash, KO, HO.—This is a very important substance, and one of great practical utility. It is always prepared for use by decomposing the carbonate by hydrate of lime, as in the following process, which is very convenient: 10 parts by carbonate of potash are dissolved in 100 parts of water, and heated to ebullition in a clean untinned iron, or, still better, silver vessel; 8 parts of good quicklime are meanwhile slaked in a covered basin, and the resulting hydrate of lime added, little by little, to the boiling solution of carbonate, with frequent stirring. When all the lime has been introduced, the mixture is suffered to boil a few minutes, and then removed from the fire, and covered up. In the course of a very short time, the solution will have become quite clear, and fit for decantation, the carbonate of lime with the excess of hydrate, settling down as a heavy, sandy precipitate. The solution should not effervesce with acids.

It is essential in this process that the solution of carbonate of potash be dilute, otherwise the decomposition becomes imperfect; the proportion of lime recommended is much greater than that required by theory, but it is always proper to have an excess.

The solution of hydrate, or as it is commonly called, caustic potash, may be concentrated by quick evaporation in the iron or silver vessel to any desired extent; when heated until vapor of water ceases to be disengaged, and then suffered to cool, it furnishes the solid hydrate, containing single equivalents of potash and water.

Pure hydrate of potash is a white solid substance, very deliquescent and soluble in water; alcohol also dissolves it freely, which is the case with comparatively few of the compounds of this base; the solid hydrate of commerce, which is very impure, may thus be purified. The solution of this substance possesses, in the very highest degree, the properties termed alkaline; it restores the blue color to litmus which has been reddened by an acid; neutralizes completely the most powerful acids; has a nauseous and peculiar taste, and dissolves the skin, and many other organic matters, when the latter are subjected to its action. It is constantly used by surgeons as a cautery, being moulded into little sticks for this purpose.

Hydrate of potash, both in the solid state and in solution, rapidly absorbs carbonic acid from the air; hence it must be kept in closely stopped bottles. When imperfectly prepared, or partially altered by exposure, it effervesces with an acid.

The water in this compound cannot be displaced by heat, the hydrate volatilizing as a whole at a very high temperature.

The following table of the densities and value in real alkali of different solutions of hydrate of potash is given on the authority of Dr. Dalton.

Density.	Per centage of real alkali.	Density.	Per centage of real alkali.
1·68	51·2	1·33	26·3
1·60	46·7	1·28	23·4
1·52	42·9	1·23	19·5
1·47	39·6	1·19	16·2
1·44	36·8	1·15	13·0
1·42	34·4	1·11	9·5
1·39	32·4	1·06	4·7
1·36	29·4		

PEROXIDE OF POTASSIUM, KO_3.—This is an orange-yellow fusible substance, generated when potassium is burned in excess of dry oxygen of gas, and also formed, to a small extent, when hydrate of potash is long exposed, in a melted state, to the air. When nitre is decomposed by a strong heat, peroxide of potassium is also produced. It is decomposed by water into potash, which unites with the latter, and into oxygen gas.

CARBONATE OF POTASH, KO,CO_2+2HO.—Salts of potash containing a vegetable acid are of constant occurrence in plants, where they perform important, but little understood, functions in the economy of those beings. The potash is derived from the soil, which, when capable of supporting vegetable life, always contains that substance. When plants are burned, the organic acids are destroyed, and the potash left in the state of carbonate.

It is by these indirect means that the carbonate, and, in fact, nearly all the salts of potash, are obtained; the great natural depository of the alkali is the felspar of granitic and other unstratified rocks, where it is combined with silica, and in an insoluble state. Its extraction thence is attended with too many difficulties to be attempted on the large scale; but when these rocks disintegrate into soils, and the alkali acquires solubility, it is gradually taken up by plants, and accumulates in their substance in a condition highly favorable to its subsequent applications.

Potash-salts are always most abundant in the green and tender parts of plants, as may be expected, since from these evaporation of nearly pure water takes place to a large extent; the solid timber of forest trees contains comparatively little.

In preparing the salt on an extensive scale, the ashes are subjected to a process called lixiviation: they are put into a large cask or tun, having an aperture near the bottom, stopped by a plug, and a quantity of water is added. After some hours the liquid is drawn off, and more water added, that the whole of the soluble matter may be removed. The weakest solutions are poured upon fresh quantities of ash, in place of water. The solutions are then evaporated to dryness, and the residue calcined, to remove a little brown organic matter; the product is the crude potash or pearlash of commerce, of which very large quantities are obtained from Russia and America.

This salt is very impure; it contains silicate and sulphate of potash, chloride of potassium, &c.

The purified carbonate of potash of pharmacy is prepared from the crude article, by adding an equal weight of cold water, agitating, and filtering; most of the foreign salts are, from their inferior degree of solubility, left behind. The solution is then boiled down to a very small bulk, and suffered to cool, when the carbonate separates in small crystals containing 2 equiv. of water, which are drained from the mother-liquor, and then dried in a stove.

A still purer salt may be obtained by exposing to a red heat purified cream of tartar (acid tartrate of potash,) and separating the carbonate by solution in water and crystallization, or evaporation to dryness.

Carbonate of potash is extremely deliquescent, and soluble in less than its own weight of water; the solution is highly alkaline to test-paper. It is insoluble in alcohol. By heat, the water of crystallization is driven off, and by a temperature of full ignition, the salt is fused, but not otherwise changed. This substance is largely used in the arts, and is a compound of great importance.

BICARBONATE OF POTASH, KO, CO_2+HO, CO_2.—When a stream of carbonic acid gas is passed through a cold solution of carbonate of potash, the gas is rapidly absorbed, and a white, crystalline, and less soluble substance separated, which is the new compound. It is collected, pressed, redissolved in warm water, and the solution left to crystallize.

Bicarbonate of potash is much less soluble than simple carbonate; it requires for that purpose 4 parts of cold water. The solution is nearly neutral to test paper, and has a much milder taste than the preceding salt. When boiled, carbonic acid is disengaged. The crystals, which are large and beautiful, derive their form from a right rhombic prism; they are decomposed by heat, water and carbonic acid being extricated, and simple carbonate left behind.

A sesqui-carbonate of potash is also said to exist.

NITRATE OF POTASH; NITRE; SALTPETRE, KO, NO_5.—This important compound is a natural product, being disengaged by a kind of efflorescence from the surface of the soil in certain dry and hot countries. It may also be produced by artificial means, namely, by the oxidation of ammonia in presence of a powerful base.

In France, large quantities of artificial nitre are prepared by mixing animal refuse of all kinds with old mortar or hydrate of lime and earth, and placing the mixture in heaps, protected from the rain by a roof, but freely exposed to the air. From time to time the heaps are watered with putrid urine, and the mass turned over, to expose fresh surfaces to the air. When much salt has been formed, the mixture is lixiviated, and the solution, which contains nitrate of lime, is mixed with carbonate of potash; carbonate of lime is formed, and the nitric acid transferred to the alkali. The filtered solution is then made to crystallize, and the crystals purified by re-solution and crystallization several times repeated.

All the nitre used in this country comes from the East Indies; it is dissolved in water, a little carbonate of potash added to precipitate lime, and then the salt purified as above.

Nitrate of potash crystallizes in anhydrous six-sided prisms, with dihedral summits; it is soluble in 7 parts of water at 60°, and in its own weight of boiling water. Its taste is saline and cooling, and it is without action on vegetable colors. At a temperature below redness it melts, and, by a strong heat, is completelely decomposed.

When thrown on the surface of many metals in a state of fusion, or when mixed with combustible matter and heated, rapid oxidation ensues, at the expense of the oxygen of the nitric acid. Examples of such mixtures are found in common gunpowder, and in nearly all pyrotechnic compositions, which burn in this manner independently of the oxygen of the air, and even under water. Gunpowder is made by very intimately mixing together nitrate of potash, charcoal, and sulphur, in proportions which approach 1 equiv. nitre, 3 eq. carbon, and 1 eq. sulphur.

These quantities give, reckoned to 100 parts, and compared with the proportions used in the manufacture of the English government powder,* the following results:—

	Theory.	Proportions in practice.
Nitrate of potash	74·8	75
Charcoal	13·3	15
Sulphur	11·9	10
	100·	100

The nitre is rendered very pure by the means already mentioned, freed from water by fusion, and ground to fine powder; the sulphur and charcoal, the latter being made from light wood, as dogwood or alder, are also finely ground, after which the materials are weighed out, moistened with water,

* Dr. M'Culloch, Ency. Brit.

and thoroughly mixed, by grinding under an edge-mill. The mass is then subjected to great pressure, and the mill-cake thus produced broken in pieces and placed in sieves made of perforated vellum, moved by machinery, each containing, in addition, a round piece of heavy wood. The grains of powder broken off by attrition, fall through the holes in the skin, and are easily separated from the dust by sifting. The powder is, lastly, dried by exposure to steam-heat, and sometimes glazed or polished by agitation in a kind of cask mounted on an axis.

When gunpowder is fired, the oxygen of the nitrate of potash is transferred to the carbon, forming carbonic oxide; the sulphur combines with the potassium, and the nitrogen is set free. The large volume of gas thus produced, and still further expanded by the very exalted temperature, sufficiently accounts for the explosive effects.

SULPHATE OF POTASH, KO, SO_3.—The acid residue left in the retort when nitric acid is prepared is dissolved in water, and neutralized with crude carbonate of potash. The solution furnishes, on cooling, hard transparent crystals of the neutral sulphate, which may be re-dissolved in boiling water, and re-crystallized.

Sulphate of potash is soluble in about 10 parts of cold, and in a much smaller quantity of boiling water; it has a bitter taste, and is neutral to test-paper. The crystals much resemble those of quartz in figure and appearance; they are anhydrous, and decrepitate when suddenly heated, which is often the case with salts containing no water of crystallization. They are quite insoluble in alcohol.

BISULPHATE OF POTASH, KO, SO_3+HO, SO_3.—The neutral sulphate in powder is mixed with half its weight of oil of vitriol, and the whole evaporated quite to dryness, in a platinum vessel, placed under a chimney; the fused salt is dissolved in hot water, and left to crystallize. The crystals have the figure of flattened rhombic prisms, and are much more soluble than the neutral salt, requiring only twice their weight of water at 60°, and less than half that quantity at 212°. The solution has a sour taste and strong acid reaction.

BISULPHATE OF POTASH, ANHYDROUS, KO, $2SO_3$.—Equal weights of neutral sulphate of potash and oil of vitriol are dissolved in a small quantity of warm distilled water, and set aside to cool. The anhydrous sulphate crystallizes out in long delicate needles, which if left several days in the mother liquor disappear, and give place to crystals of the ordinary hydrated bisulphate above described. This salt is decomposed by a large quantity of water.*

SESQUISULPHATE OF POTASH, 2 (KO, SO_3)+HO, SO_3.—A salt, crystallizing in fine needles resembling those of asbestos, and having the composition stated, was obtained by Mr. Phillips from the nitric acid residue. M. Jacquelain was unsuccessful in his attempts to reproduce this compound.

CHLORATE OF POTASH, KO, ClO_5.—The theory of the production of chloric acid, by the action of chlorine gas on a solution of caustic potash, has been already described, (p. 125.)

Chlorine gas is conducted by a wide tube into a strong and warm solution of carbonate of potash, until absorption of the gas ceases. The liquid is, if necessary, evaporated, and then allowed to cool, in order that the slightly soluble chlorate may crystallize out. The mother-liquor affords a second crop of crystals, but they are much more contaminated by chloride of potassium. It may be purified by one or two re-crystallizations.

Chlorate of potash is soluble in about 20 parts of cold, and 2 of boiling water; the crystals are anhydrous, flat, and tabular; in taste it somewhat resembles nitre. Heated, it disengages oxygen gas from both acid and base,

* Jacquelain, Ann. Chim. et Phys., vol. vii. p. 311.

and leaves chloride of potassium. By arresting the decomposition when the evolution of gas begins, and re-dissolving the salt, hyperchlorate of potash and chloride of potassium may be obtained.

This salt deflagrates violently with combustible matter, explosion often occurring by friction or blows. When about one grain weight of chlorate, and an equal quantity of sulphur are rubbed in a mortar, the mixture explodes with a loud report; hence it cannot be used in the preparation of gunpowder instead of nitrate of potash. Chlorate of potash is now a large article of commerce, being employed, together with phosphorus, in making instantaneous light matches.

Hyperchlorate of potash, KO, ClO_7. This has been already noticed under the head of hyperchloric acid. It is best prepared by projecting powdered chlorate of potash into warm nitric acid, when the chloric acid is resolved into hyperchloric acid, chlorine, and oxygen gases. The salt is separated by crystallization from the nitrate. Hyperchlorate of potash is a very feebly soluble salt; it requires 55 parts of cold water, but is more freely taken up at a boiling heat. The crystals are small, and have the figure of an octahedron with square base. It is decomposed by heat, in the same manner as chlorate of potash.

Sulphurets of potassium.—Three distinct compounds of potassium and sulphur are described, containing KS; KS_3; and KS_5.

Simple or *monosulphuret of potassium*, is formed by directly combining the metal with sulphur, or by reducing sulphate of potash at a red-heat, by hydrogen or charcoal powder. Another method is to take a strong solution of hydrate of potash, and after dividing it into two equal portions, saturate the one with sulphuretted hydrogen gas, and then add the remainder. The whole is then evaporated to dryness in a retort, and the residue fused.

The monosulphuret is a crystalline cinnabar-red mass, very soluble in water. The solution has an exceedingly offensive and caustic taste, and is decomposed by acids, even carbonic acid, with evolution of sulphuretted hydrogen, and formation of a salt of the acid used. This compound is a strong sulphur-base, and unites with the sulphurets of hydrogen, carbon, arsenic, &c., forming crystallizable saline compounds. One of these, $KS + HS$, is produced when hydrate of potash is saturated with sulphuretted hydrogen, as beforementioned.

The higher sulphurets are obtained by fusing the monosulphuret with different proportions of sulphur. They are soluble in water, and decomposed by acids, in the same manner as the foregoing compound, with this addition, that the excess of sulphur is precipitated as a fine white powder.

Hepar sulphuris is a name given to a brownish substance, sometimes used in medicine, made by fusing together different proportions of carbonate of potash and sulphur. It is a variable mixture of the two higher sulphurets with hyposulphite and sulphate of potash.

When equal parts of sulphur and dry carbonate of potash are melted together at a temperature not exceeding 482° F., the decomposition of the salt is quite complete, and all the carbonic acid is expelled. The fused mass dissolves in water, with the exception of a little mechanically-mixed sulphur, with dark brown color, and the solution is found to contain nothing besides pentasulphuret of potassium and hyposulphite of potash.

3 eq. potash {	2 eq. potassium	2 eq. pentasulphuret of potassium.
	2 eq. oxygen	
	1 eq. potash	
12 eq. sulphur {	10 eq. sulphur	
	2 eq. sulphur	1 eq. hyposulphite of potash.

When the mixture has been exposed to a temperature approaching that of ignition, it is found on the contrary to contain sulphate of potash, arising from the decomposition of the hyposulphite which then occurs.

12 eq. hyposulphite of potash { 12 eq. potash { 3 eq. potassium, 3 eq. oxygen, 9 eq. potash; 12 eq. hyposulph. acid { 15 eq. sulphur, 9 eq. sulphur, 24 eq. oxygen

3 eq. pentasulphuret of potassium.

9 eq. sulphate of potash.

From both these mixtures the pentasulphuret of potassium may be extracted by alcohol, in which it dissolves.

When the carbonate is fused with half its weight of sulphur only, then the ter- or trito-sulphuret, KS_3, is produced instead of that above indicated; 3 eq. of potash and 8 eq. of sulphur containing the elements of 2 eq. trito-sulphuret and 1 eq. hyposulphite.

The effects described happen in the same manner when hydrate of potash is substituted for the carbonate; and also when a solution of the hydrate is boiled with sulphur, a mixture of sulphuret and hyposulphite always results.*

Chloride of potassium.—KCl.—This salt is obtained in large quantity in the manufacture of chlorate of potash; it is easily purified from any portions of the latter by exposure to a dull red-heat. It is also contained in kelp, and is separated for the use of the alum-maker.

Chloride of potassium closely resembles common salt in appearance, assuming like that substance the cubic form of crystallization. The crystals dissolve in three parts of cold, and in a much less quantity of boiling water; they are anhydrous, have a simple saline taste, with slight bitterness, and fuse when exposed to a red heat. Chloride of potassium is volatilized by a very high temperature.

Iodide of potassium.—KI.—There are two different methods of preparing this important medicinal compound.

(1.) When iodine is added to a strong solution of caustic potash free from carbonate, it is dissolved in large quantity, forming a colorless solution containing iodide of potassium and iodate of potash; the reaction is the same as in the analogous case with chlorine. When the solution begins to be permanently colored by the iodine, it is evaporated to dryness, and cautiously heated red-hot; by which, the iodate of potash is entirely converted into iodide of potassium. The mass is then dissolved in water, and after filtration, made to crystallize.

(2.) Iodine, water, and iron-filings or scraps of zinc, are placed in a warm situation until the combination is complete, and the solution colorless. The resulting iodide of iron or zinc is then filtered, and exactly decomposed with solution of pure carbonate of potash, great care being taken to avoid excess of the latter. Iodide of potassium and carbonate of protoxide of iron, or zinc, are obtained; the former is separated by filtration, and evaporated until the solution is sufficiently concentrated to crystallize on cooling, the washings of the filter being added to avoid loss.

Iodide of iron { Iodine, Iron

Carbonate of potash { Potash { Potassium, Oxygen; Carbonic acid

Iodide of potassium.

Carbonate of protoxide of iron.

* Mitcherlich, Lehrbuch der Chemie, ii. p. 47.

The second method is on the whole to be preferred.

Iodide of potassium crystallizes in cubes, which are often, from some unexplained cause, milk-white and opaque; they are anhydrous, and fuse readily when heated. The salt is very soluble in water, but not deliquescent, when pure, in a moderately dry atmosphere; it is dissolved by alcohol.

Solution of iodide of potassium, like those of all the soluble iodides, dissolves a large quantity of free iodine, forming a deep brown liquid, not decomposed by water.

Bromide of Potassium.—KBr.—This compound may be obtained by processes exactly similar to those just described, substituting bromine for the iodine. It is a colorless and very soluble salt, quite indistinguishable in appearance and general characters from the iodide.

The salts of potash are colorless, when not associated with a colored metallic oxide or acid. They are all more or less soluble in water, and may be distinguished by the following characters:—

(1.) Solution of tartaric acid added to a moderately-strong solution of a potash salt, gives after some time a white, crystalline precipitate of cream of tartar; the effect is greatly promoted by strong agitation.

(2.) Solution of chloride of platinum gives under similar circumstances, a crystalline yellow precipitate, which is a double salt of chloride of platinum and chloride of potassium. Both this compound and cream of tartar are, however, soluble in about sixty parts of cold water. An addition of alcohol increases the delicacy of both tests.

(3.) Perchloric acid, and hydrofluosilicic acid, give rise to slightly soluble precipitates when added to a potash-salt.

(4.) Salts of potash usually color the outer blow-pipe flame purple or violet.

SODIUM.

This metal was obtained by Davy very shortly after the discovery of potassium, and by similar means. It may be prepared in large quantity by decomposing carbonate of soda by charcoal at a high temperature.

Six parts of anhydrous carbonate of soda are dissolved in a little hot water, and mixed with two parts of finely-powdered charcoal and one part of charcoal in lumps. The whole is then evaporated to dryness, transferred to the iron retort before described, and heated in the same manner to whiteness. A receiver containing rock-oil is adapted to the tube, and the whole operation carried on in the same way as when potassium is made. The process, when well conducted, is said to be easy and certain.

Sodium is a silver-white metal, greatly resembling potassium in every respect; it is soft at common temperatures, melts at 194°, and oxidizes very rapidly in the air. Its specific gravity is ·972. Placed upon the surface of cold water, sodium decomposes that liquid with great violence, but seldom takes fire unless the motions of the fragment be restrained, and its rapid cooling diminished, by adding gum or starch to the water. With hot water it takes fire at once, burning with a bright yellow flame, and giving rise to a solution of soda.

The equivalent of sodium is 23·27, and its symbol (Natrium) Na.

There are two well-defined compounds of sodium and oxygen; the protoxide, anhydrous soda, NaO, and the peroxide, NaO_2, or perhaps, NaO_3; they are formed by burning sodium in air or oxygen gas, and resemble in every respect the corresponding compounds of potassium.

Hydrate of Soda.—NaO, HO.—This substance is prepared in practice by

decomposing a somewhat dilute solution of carbonate of soda by hydrate of lime; the description of the process employed in the case of hydrate of potash, and the precautions necessary, apply word for word to that of soda.

The solid hydrate is a white, fusible substance, very similar in properties to hydrate of potash. It is deliquescent, but dries up again after a time in consequence of the absorption of carbonic acid. The solution is highly alkaline, and a powerful solvent for animal matter; it is used in large quantity for making soap.

The strength of a solution of caustic soda may be roughly determined from a knowledge of its density, by the aid of the following table drawn up by Dr. Dalton.

TABLE OF DENSITY.

Density.	Per centage of real soda.	Density.	Per centage of real soda.
2·00	77·8	1·40	29·0
1·85	63·6	1·36	23·0
1·72	53·8	1·32	23·0
1·63	46·6	1·29	19·0
1·55	41·2	1·23	16·0
1·50	36·8	1·18	13·0
1·47	34·0	1·12	9·0
1·44	31·0	1·06	4·7

CARBONATE OF SODA.—NaO, CO_2+10HO. Carbonate of soda was once exclusively obtained from the ashes of sea-weeds, and of plants, such as the *salsola soda*, which grew by the sea-side, or being cultivated in suitable localities for the purpose, were afterwards subjected to incineration. The *barilla* yet employed in soap-making, is thus produced in several places on the coast of Spain, as Alicant, Carthagena, &c. That made in Brittany is called *varec*.

Carbonate of soda is now manufactured on a stupendous scale from common salt, or rather from sulphate of soda, by a process of which the following is an outline—

A charge of 600 lbs. of common salt* is placed upon the hearth of a well-heated reverberatory furnace, and an equal weight of sulphuric acid of sp. gr. 1·6 poured upon it through an opening in the roof, and thoroughly mingled with the salt; hydrochloric acid gas is disengaged, which is usually allowed to escape by the chimney, and the salt is converted into sulphate of soda. This part of the process takes for completion about four hours, and requires much care and skill.

The sulphate is next reduced to powder and mixed with an equal weight of chalk or limestone, and half as much small coal, both ground or crushed. The mixture is thrown into a reverberatory furnace, and heated to fusion, with constant stirring; 2 cwt. is about the quantity operated on at once. When the decomposition is judged complete, the melted matter is raked from the furnace into an iron trough, where it is allowed to cool. When cold it is broken up into little pieces and lixiviated with cold or tepid water. The solution is evaporated to dryness and the salt calcined with a little saw-dust in a suitable furnace. The product is the soda-ash, or British alkali of commerce, which, when of good quality, contains from 48 to 52 per cent. of pure soda, partly in the state of carbonate, and partly as hydrate, the remainder being chiefly sulphate of soda and common salt, with occasional traces of sulphite or hyposulphite, and also cyanide of sodium. By dissolving soda-ash in hot

* Graham, Elements, p. 333.

water, filtering the solution, and then allowing it to cool slowly, the carbonate is deposited in large transparent crystals.

The reaction which takes place in the calcination of the sulphate with chalk and coal-dust seems to consist, first, in the conversion of the sulphate of soda into sulphuret of sodium by the aid of the combustible matter, and secondly, in the double interchange of elements between that substance and the carbonate of lime.

Sulphuret of sodium { Sulphur, Sodium } — Carbonate of soda.
Carbonate of lime { Lime { Calcium, Oxygen }, Carbonic acid } — Sulphuret of Calcium.

The sulphuret of calcium combines with another proportion of lime to form a peculiar compound, which is insoluble in cold or slightly warm water.

Other processes have been proposed, and even carried into execution, but the above is found most advantageous.

The ordinary crystals of carbonate of soda contain ten equivalents of water, but by particular management the same salt may be had with seven equivalents, or sometimes with only one,—these differ in figure from the preceding. The common form of the crystal is derived from an oblique rhombic prism; they effloresce in dry air, and crumble to white powder. Heated, they fuse in their water of crystallization: when the latter has been expelled, and the dry salt exposed to a full red-heat, it melts without undergoing change. The common crystals dissolve in two parts of cold, and in less than their own weight of boiling water; the solution has a strong, disagreeable, alkaline taste, and a powerful alkaline reaction.

Bicarbonate of Soda.—$NaO, CO_2 + HO, CO_2$.—This salt is prepared by passing carbonic acid gas into a cold solution of the neutral carbonate, or by placing the crystals in an atmosphere of the gas, which is rapidly absorbed, while the crystals lose the greater part of their water, and pass into the new compound.

Bicarbonate of soda, prepared by either process, is a crystalline white powder, which cannot be re-dissolved in warm water without partial decomposition. It requires 10 parts of water at 60° for solution; the liquid is feebly alkaline to test-paper, and has a much milder taste than that of the simple carbonate. It does not precipitate a solution of magnesia. By exposure to heat, the salt is converted into neutral carbonate.

A sesquicarbonate of soda containing $2NaO, 3CO_2 + 4HO$ has been described by Mr. Phillips; like the sesquicarbonate of potash, it cannot be formed at pleasure. This salt occurs native on the banks of the soda-lakes of Sakena in Africa, whence it is exported under the name of Trona.

Alkalimetry; analysis of hydrates and carbonates of the alkalies.—The general principle of these operations consists in ascertaining the quantity of real alkali in a given weight of the substance examined by finding how much of the latter is required to neutralize a known quantity of an acid, as sulphuric acid.

The first step is the preparation of a stock of dilute sulphuric acid of determinate strength; containing, for example, 100 grains of real acid in every 1000 grain-measures of liquid;* a large quantity, as a gallon or more, may be pre-

* The capacity of 1000 grains of distilled water at 60°. The grain-measure of water is often found a very convenient and useful unit of volume in chemical researches. Vessels graduated on this plan bear simple comparison with the imperial gallon and pint, and frequently also enable the operator to measure out a liquid of known density instead of weighing it.

pared at once by the following means. The oil of vitriol is first examined; if it be good and of the sp. gr. 1·85 or near it, the process is extremely simple; every 49·09 grains of the liquid acid contains 40·09 grains of absolute acid; the quantity of the latter required in the gallon, or, 70·000 grain-measures of dilute acid will be of course 7000 grains. This is equivalent to 8571 grains of the oil of vitriol, for

Real acid.		Oil of vitriol.				
40·09	:	49·09	: :	7000	:	8571.

All that is required to be done, therefore, is to weigh out 8571 grains of oil of vitriol, and dilute it with so much water, *that the mixture, when cold, shall measure exactly one gallon.*

If very often happens, however that the oil of vitriol to be used is not so strong as that above-mentioned; in which case it is necessary to discover its real strength, as estimated from its saturating power. Pure anhydrous carbonate of soda is prepared by heating to dull redness, without fusion, the bicarbonate; of this salt 53·27 grains, or 1 eq., correspond to 31·27 grains of soda, and neutralize 40·09 grains of real sulphuric acid.

A convenient quantity is carefully weighed out, and added little by little to a known weight, say 100 grains, of the oil of vitriol to be tried, diluted with four or five times its weight of water, until the liquid becomes quite neutral to test-paper. By weighing again the residue of the carbonate, it is at once known how much of the latter has been employed; the amount of real acid in the hundred parts of oil of vitriol is then easily calculated. Thus, suppose the quantity of carbonate of soda used to be 105 grains; then,

Fig. 138.

Carb. soda.		Sulph. acid.				
53·27	:	40·09	: :	105	:	79.

79 grains of real acid are consequently contained in 100 grains of oil of vitriol; consequently,

79 : 100 : : 7000 : 8861,

the weight in grains of the oil of vitriol required to make one gallon of the dilute acid.

The "alkalimeter" is next to be constructed. This is merely a 1000-grain measure, made of a piece of even, cylindrical glass tube, about 15 inches long and ·6 inch internal diameter, closed at one extremity, and moulded into a spout or lip at the other. A strip of paper is pasted on the tube and suffered to dry, after which the instrument is graduated by counterpoising it in a nearly upright position in the pan of a balance of moderate delicacy, and weighing into it, in succession, 100, 200, 300, &c., grains of distilled water at 60°, until the whole quantity, amounting to 1000 grains, has been introduced, the level of the water in the tube being, after each addition, carefully marked with a pen upon the strip of paper, while the tube is held quite upright, and the mark made between the top and bottom of the curve formed by the surface of the water. The smaller divisions of the scale, of 10 grains each, may then be made by dividing by compasses each of the spaces into 10 equal parts. When the graduation is complete, and the operator is satisfied with its accuracy, the marks may be transferred to the tube itself by a sharp file, and the paper removed by a little tepid water. The numbers are scratched on the glass with the hard end of the same file. When this alkalimeter is used with the dilute acid described, every division of the glass will correspond to one grain of real sulphuric acid.

Let it be required, by way of example, to test the commercial value of soda-ash, or to examine it for scientific purposes: 50 grains of the sample are weighed out, dissolved in a little warm water, and, if necessary, the solution filtered; the alkalimeter is then filled to the top of the scale with the test-acid, and the latter poured from it into the alkaline solution, which is tried from time to time with red litmus paper. The addition of acid must of course be made very cautiously as neutralization advances. When the solution, after being heated a few minutes, no longer affects either blue or red test-paper, the measure of liquid employed is read off, and the quantity of soda present in the state of carbonate or hydrate in the 50 grains of salt, found by the rule of proportion. Suppose 33 measures, consequently 33 grains of acid, have been taken; then,

Sulph. acid.		Soda.				
40·09	:	31·27	: :	33	:	25·6:

The sample contains, therefore, 51·2 per cent. of available alkali.

It will be easily seen that the principle of the process described admits of very wide application, and that by the aid of the alkalimeter and carefully prepared test-acid, the hydrates and carbonates of potash, soda, and ammonia, both in the solid state and in solution, can be examined with great ease and accuracy. The quantity of real alkali in a solution of caustic ammonia may thus be determined, the equivalent of that substance, and the amount of acid required to neutralize a known weight, being inserted in the second and third terms in the above Rule-of-three statement. The same acid answers for all.

It is often desirable in the analysis of carbonates, to determine directly the proportion of carbonic acid; the following method leaves nothing to be desired in point of precision:—

A small light glass flask of three or four ounces capacity, with lipped edge, is chosen, and a cork fitted to it. A piece of tube about three inches long is drawn out at one extremity, and fitted, by means of a small cork and a bit of bent tube, to the cork of the flask. This tube is filled with fragments of chloride of calcium, prevented from escaping by a little cotton at either end; the joints are secured by sealing-wax. A short tube, closed at one extremity, and small enough to go into the flask, is also provided, and the apparatus is complete. Fifty grains of the carbonate to be examined are carefully weighed out and introduced into the flask, together with a little water; the small tube is then filled with oil of vitriol, and placed in the flask in a nearly upright position, and leaning against its side in such a manner that the acid does not escape. The cork and chloride of calcium tube are then adjusted, and the whole apparatus accurately counterpoised on the balance. This done, the flask is slightly inclined, so that the oil of vitriol may slowly mix with the other substances and decompose the carbonate, the gas from which escapes in a dry state from the extremity of the tube. When the action has entirely ceased, the liquid is heated until it boils, and the steam begins to condense in the drying-tube; it is then left to cool, and weighed, when the loss indicates the quantity of carbonic acid. The acid must be in excess after the experiment. When carbonate of lime is thus analyzed, strong hydrochloric acid must be substituted for the oil of vitriol.

Fig. 139.

Sulphate of soda, Glauber salt, NaO, SO_3+10HO.—This is a by-product in several chemical operations; it may of course be prepared directly, if wanted pure, by adding dilute sulphuric acid to saturation, to a solution of carbonate of soda. It crystallizes in a figure derived from an oblique rhombic

prism; the crystals contain 10 eq. of water, are efflorescent, and undergo watery fusion when heated, like those of the carbonate; they are soluble in twice their weight of cold water, and rapidly increase in solubility as the temperature of the liquid rises to 91°.5 F. when a maximum is reached, 100 parts of water dissolving 322 parts of the salt. Heated beyond this point, the solubility diminishes, and a portion of sulphate is deposited. A warm saturated solution, evaporated at a high temperature, deposits opaque prismatic crystals, which are anhydrous. This salt has a slightly bitter taste, and is purgative. Mineral springs sometimes contain it, as at Cheltenham.

Bisulphate of soda, NaO, SO_3+HO, SO_3+3HO.—This is prepared by adding to 10 parts of anhydrous neutral sulphate, 7 of oil of vitriol, evaporating the whole to dryness, and gently igniting. The bisulphate is very soluble in water, and has an acid reaction. It is not deliquescent. When very strongly heated, the fused salt gives an anhydrous sulphuric acid, and becomes simple sulphate; a change which necessarily supposes the previous formation of a true anhydrous bisulphate, NaO, $2SO_3$.

Hyposulphite of soda, NaO, S_2O_2.—There are several modes of procuring this salt, which is now used in considerable quantity for photographic purposes. One of the best is to form neutral *sulphite* of soda, by passing a stream of well washed sulphurous acid gas into a strong solution of carbonate of soda, and then to digest the solution with sulphur at a gentle heat during several days. By careful evaporation at a moderate temperature the salt is obtained in large and regular crystals, which are very soluble in water.

Nitrate of soda; cubic nitre, NaO, NO_5.—Nitrate of soda occurs native, and in enormous quantity, at Atacama in Peru, where it forms a regular bed, of great extent, covered with clay and alluvial matter. The pure salt commonly crystallizes in rhombohedrons, resembling those of calcareous spar, but is probably dimorphous. It is deliquescent, and very soluble in water. Nitrate of soda is employed for making nitric acid, but cannot be used for gunpowder, as the mixture burns too slowly, and becomes damp in the air. It has been lately used with some success in agriculture as a superficial manure or top-dressing.

Phosphates of soda; common tribasic phosphate, 2NaO, HO, PO_5+24HO.—This beautiful salt is prepared by precipitating the acid phosphate of lime obtained by decomposing bone-earth by sulphuric acid, with a slight excess of carbonate of soda. It crystallizes in oblique rhombic prisms, which are efflorescent. The crystals dissolve in 4 parts of cold water, and undergo the aqueous fusion when heated. The salt is bitter and purgative; its solution is alkaline to test-paper. Crystals containing 14 equivalents of water, and having a form different from that above mentioned, have been obtained.

A second tribasic phosphate, sometimes called sub-phosphate, 3NaO, PO_5+24HO, is obtained by adding solution of caustic soda to the preceding salt. The crystals are slender six sided prisms, soluble in 5 parts of cold water. It is decomposed by acids, even carbonic, but suffers no change by heat, except the loss of its water of crystallization. Its solution is strongly alkaline. A third tribasic phosphate, often called super-phosphate or bi-phosphate, NaO, 2HO, PO_5+2HO, may be obtained by adding phosphoric acid to the ordinary phosphate, until it ceases to precipitate chloride of barium, and exposing the concentrated solution to cold. The crystals are prismatic, very soluble, and have an acid reaction. When strongly heated, the salt becomes changed into monobasic phosphate of soda.

Tribasic phosphate of soda, ammonia, and water; microcosmic salt, NaO, NH_4O, HO, PO_5+8HO.—Six parts of common phosphate of soda are heated with 2 of water until the whole is liquefied, when 1 part of powdered sal-ammoniac is added; common salt separates, and may be removed by a filter, and

from the solution, duly concentrated, the new salt is deposited in prismatic crystals, which may be purified by one or two recrystallizations. Microcosmic salt is very soluble. When gently heated, it parts with the 8 eq. of water of crystallization, and, at a higher temperature, that in the base is expelled, together with the ammonia, and a very fusible compound, metaphosphate of soda, remains, which is valuable as a flux in blow-pipe experiments. This salt is said to occur in the urine.

BIBASIC PHOSPHATE OF SODA; PYROPHOSPHATE OF SODA, $2NaO,PO_5+10HO$.—Prepared by strongly heating common phosphate of soda, dissolving the residue in water, and recrystallizing. The crystals are very brilliant, permanent in the air, and less soluble than the original phosphate; their solution is alkaline. A bibasic phosphate, containing an equivalent of basic water, has been obtained; it does not, however, crystallize.

MONOBASIC PHOSPHATE OF SODA; METAPHOSPHATE OF SODA, NaO, PO_5.—Obtained by heating either the acid tribasic phosphate, or microcosmic salt. It is a transparent, glassy substance, fusible at a dull red-heat, deliquescent, and very soluble in water. It refuses to crystallize, but dries up into a gum-like mass.

The tribasic phosphates give a bright yellow precipitate with solution of nitrate of silver; the bibasic and monobasic phosphates, afford white precipitates with the same substances. The salts of the two latter classes, fused with excess of carbonate of soda, yield the tribasic modification of the acid.

BIBORATE OF SODA; BORAX, $NaO, 2BO_3+10HO$.—This compound occurs in the waters of certain lakes in Thibet and Persia; it is imported in a crude state from the East Indies under the name of *tinçal*. When purified, it constitutes the borax of commerce. Much borax is now, however, manufactured from the native boracic acid of Tuscany. Borax crystallizes in six-sided prisms, which effloresce in dry air, and require 20 parts of cold, and 6 of boiling water for solution. Exposed to heat, the 10 eq. of water of crystallization are expelled, and at a higher temperature the salt fuses, and assumes a glassy appearance on cooling; in this state it is much used for blow-pipe experiments. By particular management, crystals of borax can be obtained with 5 eq. of water; they are very hard, and permanent in the air. Although by constitution an acid salt, borax has an alkaline reaction to test-paper. It is used in the arts in soldering metals, and sometimes enters into the composition of the glaze with which stone-ware is covered.

Neutral borate of soda may be formed by fusing together borax and carbonate of soda in equivalent proportions, and then dissolving the mass in water. The crystals are large, and contain NaO, BO_3+8HO.

SULPHURET OF SODIUM, NaS.—Prepared in the same manner as the monosulphuret of potassium; it separates from a concentrated solution in octahedral crystals, which are rapidly decomposed by contact of air into a mixture of hydrate and hyposulphite of soda. It forms double sulphur salts, with sulphuretted hydrogen, bisulphuret of carbon, and other sulphur-acids.

Sulphuret of sodium is supposed to enter into the composition of the beautiful pigment *ultramarine*, prepared from the *lapis lazuli*, and which is now imitated by artificial means.*

CHLORIDE OF SODIUM; COMMON SALT, NaCl.—This very important substance is found in many parts of the world in solid beds or irregular strata of immense thickness, as in Cheshire, for example, in Spain, Poland, and many other localities. An inexhaustible supply exists also in the waters of the ocean, and large quantities are annually obtained from saline springs.

The rock-salt is almost always too impure for use; if no natural brine

* See Pharmaceutical Journal, ii. p. 53.

spring exist, an artificial one is formed by sinking a shaft into the rock-salt, and, if necessary, introducing water. This, when saturated, is pumped up, and evaporated more or less rapidly in large iron pans. As the salt separates, it is removed from the bottom of the vessels by means of a scoop, pressed while still moist into moulds, and then transferred to the drying stove. When large crystals are required, as for the coarse-grained *bay-salt* used in curing provisions, the evaporation is slowly conducted. Common salt is apt to be contaminated with chloride of magnesium.

When pure, this substance is not deliquescent in moderately dry air. It crystallizes in anhydrous cubes, which are often grouped together into pyramids, or steps. It requires about 2½ parts of water at 60° for solution, and its solubility is not sensibly increased by heat; in alcohol it is insoluble. Chloride of sodium fuses at a red heat, and is volatile at a still higher temperature. The economical uses of common salt are well known.*

The *iodide* and *bromide of sodium* much resemble the corresponding potassium compounds; they crystallize in cubes which are anhydrous, and are very soluble in water.

There is no precipitant for soda, all the salts being soluble; its presence is often determined by purely negative evidence.† The yellow color imparted by soda-salt to the outer flame of the blow-pipe, and to combustible matter, is a character of some importance.

AMMONIUM.

In connection with the compounds of potassium and sodium, those formed by ammonia are most conveniently studied. Ammoniacal salts correspond in every respect in constitution with those of potash and soda; in all cases the substance which replaces those alkalies is hydrate of ammonia, or, as it is now almost generally considered, the oxide of a hypothetical substance called ammonium, capable of playing the part of a metal, and isomorphous with potassium and sodium.

All attempts to isolate this substance have failed, apparently from its tendency to separate into ammonia and hydrogen gas. When a globule of mercury is placed on a piece of moistened caustic potash, and connected with the negative side of a voltaic battery of very moderate power, while the circuit is completed through the platinum plate upon which rests the alkali, decomposition of the latter takes place, and an amalgam of potassium is rapidly formed.

If this experiment be now repeated with a piece of sal-ammoniac instead of hydrate of potash, a soft-solid, metalline mass is also produced, which has been called the *ammoniacal amalgam*, and considered to contain ammonium in combination with mercury. A still simpler method of preparing this extraordinary compound is the following: A little mercury is put into a test-tube with a grain or two of potassium or sodium, and heat applied; combination ensues, attended by heat and light. When cold, the fluid amalgam is put into a capsule, and covered with a strong solution of sal-ammoniac. The production of ammoniacal amalgam instantly commences, the mercury increases prodigiously in volume, and becomes quite pasty. The increase of weight is, however, quite trifling; it varies from $\frac{1}{1800}$th to $\frac{1}{1200}$th part.

Left to itself, the amalgam quickly decomposes into fluid mercury, ammonia, and hydrogen.

* For Chloride of Soda, see Chloride of Lime.

† Antimoniate of potassa yields an insoluble white precipitate when added to salts of soda, forming antimoniate of soda.—R. B.

It is difficult to offer any opinion concerning the real nature of this compound; something analogous occurs when pure silver is exposed to a very high temperature, much above its melting-point, in contact with air or oxygen gas; the latter is absorbed in very large quantity, amounting, according to the observation of Gay-Lussac to 20 times the volume of the silver, and is again disengaged on reduction of the heat. The metal loses none of its lustre, and is not sensibly altered in other respects.

The great argument in favor of the existence of ammonium is founded on the perfect comparison which the ammoniacal salts bear with those of the alkaline metals.

The equivalent of ammonium is 18·06; its symbol is NH_4.

Chloride of ammonium; sal-ammoniac, NH_4Cl.—Sal-ammoniac was formerly obtained from Egypt, being extracted by sublimation from the soot of camel's dung; it is now largely manufactured from the ammoniacal liquid of the gas-works, and from the condensed products of the distillation of bones and other animal refuse, in the preparation of animal charcoal.

These impure and highly offensive solutions are treated with slight excess of hydrochloric acid, by which the free alkali is neutralized, and the carbonate and sulphuret decomposed with evolution of carbonic acid and sulphuretted hydrogen gases. The liquid is evaporated to dryness, and the salt carefully heated, to expel or decompose the tarry matter; it is then purified by sublimation in large iron vessels lined with clay, surmounted with domes of lead.

Sublimed sal-ammoniac has a fibrous texture; it is tough, and difficult to powder.

When crystallized from water it separates, under favorable circumstances, in distinct cubes or octahedrons; but the crystals are usually small, and aggregated together in rays. It has a sharp saline taste, and is soluble in 2¾ parts of cold, in a much smaller quantity of hot water. By heat, it is sublimed without decomposition. The crystals are anhydrous.

Sulphate of oxide of ammonium; sulphate of ammonia, NH_4O, SO_3+HO.—Prepared by neutralizing carbonate of ammonia by sulphuric acid, or on a large scale, by adding sulphuric acid in excess to the coal-gas liquor just mentioned, and purifying the product by suitable means. It is soluble in 2 parts of cold water, and crystallizes in long, flattened, six-sided prisms, which lose an equivalent of water when heated. It is entirely decomposed, and driven off by ignition, and, even to a certain extent, by long boiling with water, ammonia being expelled and the liquid rendered acid.

Carbonates of ammonia.—These compounds have been carefully examined by Professor Rose, of Berlin,* and appear very numerous. The *neutral anhydrous carbonate*, NH_3, CO_2, is prepared by the direct union of carbonic acid with ammoniacal gas, both being carefully cooled. The gases combine in the proportions of one measure of the first to two of the second, and give rise to a pungent, and very volatile compound, which condenses in white flocks. It is very soluble in water. The pungent, transparent carbonate of ammonia of pharmacy, which is prepared by subliming a mixture of sal-ammoniac and chalk, always contains less base than that required to form a neutral carbonate. Its composition varies a good deal, but in freshly-prepared specimens *approaches* that of a sesquicarbonate of oxide of ammonium, $2NH_4O, 3CO_2$.—When heated in a retort, the neck of which dips into mercury, it is decomposed, with disengagement of pure carbonic acid, into neutral hydrated carbonate of ammonia, and several other compounds. Exposed to the air at common temperatures, it disengages ammonia, loses its pungency, and crumbles down to a soft, white powder, which is a bicarbonate containing NH_4O, CO_2

* Annalen der Pharmacie, xxx. p. 45.

$+HO, CO_2$. This is a permanent combination, although still volatile. When a strong solution of the commercial sesquicarbonate is made with tepid water, and filtered, warm, into a close vessel, large and regular crystals of bicarbonate, having the above composition, are sometimes deposited after a few days.

These are inodorous, quite permanent in the air, and resemble, in the closest manner, crystals of bicarbonate of potash.

NITRATE OF OXIDE OF AMMONIUM; NITRATE OF AMMONIA, NH_4O, NO_5.— Easily prepared by adding carbonate of ammonia to slightly diluted nitric acid until neutralization has been reached. By slow evaporation at a moderate temperature, it crystallizes in six-sided prisms, like those of nitrate of potash, but, as usually prepared for making nitrous oxide, by quick boiling, until a portion solidifies completely on cooling, it forms a fibrous and indistinctly crystalline mass.

Nitrate of ammonia dissolves in 2 parts of cold water, is but feebly deliquescent, and deflagrates like nitre on contact with heated combustible matter. Its decomposition by heat has been already explained.*

SULPHURETS OF AMMONIUM.—Several of these compounds exist, which may be formed by distilling with sal-ammoniac the corresponding sulphurets of potassium or sodium.

The *double sulphuret of ammonium and hydrogen*, NH_4S+HS, commonly called hydrosulphate or hydrosulphuret of ammonia, is a compound of great practical utility; it is obtained by saturating a solution of ammonia with well-washed sulphuretted hydrogen gas, until no more of the latter is absorbed. The solution is nearly colorless at first, but becomes yellow after a time, without, however, suffering material injury, unless it has been exposed to the air. It gives precipitates with most metallic solutions, which are very often characteristic, and is of great service in analytical chemistry.

When dry ammoniacal gas is brought in contact with anhydrous sulphuric acid, a white crystalline compound is produced, which is soluble in water. In a freshly-prepared cold solution of this substance neither sulphuric acid nor ammonia can be found; but after standing some time, and especially if heat be applied, it passes into ordinary sulphate of ammonia.

A compound of dry ammoniacal gas and sulphurous acid also exists; it is a yellow soluble substance, altogether distinct from sulphite of ammonia. Dry carbonic acid and ammonia also unite to form a volatile white powder, as already mentioned.

When certain salts, especially chlorides in an anhydrous state, are exposed to ammoniacal gas, the latter is absorbed with great energy, and combinations formed not always easily decomposed by heat. The chlorides of copper and silver absorb, in this manner, large quantities of the gas. All these compounds must be carefully distinguished from the true ammoniacal salts containing ammonium or its oxide.

* PHOSPHATES OF OXIDE OF AMMONIUM; COMMON TRIBASIC PHOSPHATE, $2NH_4O, HO. PO_5+HO$.—This salt is formed by precipitating the acid phosphate of lime with an excess of carbonate of ammonia. The solution is allowed to evaporate spontaneously or by a gentle heat. In the latter case ammonia is lost and it becomes necessary to saturate the acid set free, previous to crystallization. It crystallizes in six-sided tables derived from oblique quadrangular prisms. Its crystals are efflorescent, soluble in alcohol, and soluble in four times its weight of cold water. Its solution has an alkaline, slightly saline taste and alkaline reaction. By heat ammonia is disengaged.

The acid tribasic phosphate, $NH_4O, 2HO, PO_5+4HO$, is formed when a solution of the common phosphate is boiled as long as ammonia is given off. It crystallizes in four-sided prisms. Its crystals are permanent, soluble in 5 parts of cold water, acid in taste and reaction.

Another tribasic phosphate, $3NH_4O, PO_5$. subphosphate, is formed by adding ammonia to either of the above. It falls as a slightly soluble granular precipitate.—R. B.

There is supposed to be yet another compound of hydrogen and nitrogen to which the term *amidogen* has been given, and to which the properties of a salt-radical are ascribed. When potassium is heated in the vapor of water, this substance is decomposed, hydrogen is evolved, and the metal converted into oxide. When the same experiment is made with dry ammoniacal gas, hydrogen is also set free, and an olive-green crystalline compound is produced, supposed to contain potassium in union with a new body, NH_2, having an equivalent of hydrogen less than ammonia.

When ammonia is added to a solution of corrosive sublimate, a white precipitate is obtained, which has been long known in pharmacy. Dr. Kane infers, from his experiments, that this substance should be looked upon as a compound of chloride of mercury with amide of mercury. The latter salt has not been obtained separately; still less has amidogen itself been isolated.

It is thought that ammonia may be considered an amide of hydrogen, analogous to water or oxide of hydrogen, capable of entering into combination with salts, and other substances, in a similar manner, yielding instable and easily-decomposed compounds, which offer a great contrast to those of the energetic *quasi*-metal ammonium.

The ammoniacal salts are easily recognized; they are all decomposed or volatilized by a high temperature; and when heated with hydrate of lime, or solution of alkaline carbonate, evolve ammonia, which may be known by its odor and alkaline reaction. The salts are all more or less soluble, the acid tartrate of ammonia and the double chloride of ammonium and platinum being among the least so; hence the salts of ammonia cannot be distinguished from those of potash by the tests of tartaric acid and platinum-solution.

LITHIUM.

A connecting link between this class of metals and the next succeeding. Lithium is obtained by electrolyzing, in contact with mercury, the hydrate of lithia, and then decomposing the amalgam by distillation. It is a white metal-like sodium, and very oxidable. The equivalent of lithium is 6·43, and its symbol, L.

The oxide, lithia, LO, is found in petalite, spodumene, lepidolite, and a few other minerals, and sometimes occurs in minute quantities in mineral springs. From petalite it may be obtained, on the small scale, by the following process: The mineral is reduced to an exceedingly fine powder, mixed with five or six times its weight of pure carbonate of lime, and the mixture heated to whiteness, in a platinum crucible, placed within a well-covered earthen one, for twenty minutes or half an hour. The shrunken coherent mass is digested in dilute hydrochloric acid, the whole evaporated to dryness, acidulated water added, and the silica separated by a filter. The solution is then mixed with carbonate of ammonia in excess, boiled, and filtered; the clear liquid is evaporated to dryness, and gently heated in a platinum crucible, to expel the sal-ammoniac. The residue is then wetted with oil of vitriol, gently evaporated once more to dryness, and ignited; pure fused sulphate of lithia remains.

This process will serve to give a good idea of the general nature of the operation by which alkalies are extracted in mineral analysis, and their quantities determined.

The hydrate of lithia is much less soluble in water than those of potash and soda; the carbonate and phosphate are also sparingly soluble salts. The chloride crystallizes in anhydrous cubes which are deliquescent. Sulphate of lithia is a very beautiful salt; it crystallizes in lengthened prisms containing one equivalent of water.

The salts of lithia color the outer flame of the blow-pipe carmine-red.

SECTION II.

METALS OF THE ALKALINE EARTHS.

BARIUM.

Barium was obtained by Sir H. Davy by means similar to those mentioned in the case of lithium; it is procured more advantageously, by strongly heating baryta in an iron tube, through which the vapor of potassium is conveyed. The reduced barium is extracted by quicksilver, and the amalgam distilled in a small green glass retort.

Barium is a white metal, having the color and lustre of silver; it is malleable, melts below a red heat, decomposes water, and gradually oxidizes in the air.

The equivalent of this metal has been fixed at 68·55; its symbol is Ba.

Protoxide of barium; baryta. BaO.—Baryta* or barytes, occurs in nature in considerable abundance as carbonate and sulphate, forming the *vein-stone* in many lead mines; from both these sources it may be extracted with facility. The best method of preparing pure baryta is to decompose the crystallized nitrate by heat in a capacious crucible of porcelain; the nitric acid is resolved into nitrous acid and oxygen, and the baryta remains behind in the form of a grayish spongy mass, fusible at a high degree of heat. When moistened with water, it combines to a hydrate with great elevation of temperature.

The hydrate is a white, soft powder, having a great attraction for carbonic acid, and soluble in 20 parts of cold and 3 of boiling water; a hot saturated solution deposits crystals on cooling, which contain $BaO, HO+9HO$. Solution of hydrate of baryta is a valuable re-agent; it is highly alkaline to test-paper, and instantly rendered turbid by the smallest trace of carbonic acid.

Peroxide of barium. BaO_2.—This may be formed, as already mentioned, by exposing baryta heated to full redness in a porcelain tube, to a current of pure oxygen gas. The peroxide is gray, and forms a white hydrate with water, which is not decomposed by that liquid in the cold, but dissolves in small quantity. The peroxide may also be made by heating pure baryta to redness in a platinum crucible, and then gradually adding an equal weight of chlorate of potash; peroxide of barium and chloride of potassium are produced. The latter may be extracted by cold water, and the peroxide left in the state of hydrate. It is interesting chiefly in its relation to peroxide of hydrogen.

Chloride of barium. $BaCl+2HO$.—This valuable salt is prepared by dissolving the native carbonate in hydrochloric acid, filtering the solution and evaporating until a skin begins to form at the surface; the solution on cooling deposits crystals. When native carbonate cannot be procured, the native sulphate may be employed in the following manner:—The sulphate is reduced to fine powder, and intimately mixed with one-third of its weight of powdered coal; the mixture is pressed into an earthen crucible to which a

* From βαρύς, heavy, in allusion to the great specific gravity of the native carbonate and sulphate.

cover is fitted, and exposed for an hour or more to a high red-heat, by which the sulphate is converted into sulphuret at the expense of the combustible matter of the coal. The black mass obtained is powdered and boiled in water, by which the sulphuret is dissolved; the solution is filtered hot, and mixed with a slight excess of hydrochloric acid; chloride of barium and sulphuretted hydrogen are produced, the latter escaping with effervescence. Lastly, the solution is filtered to separate any little insoluble matter, and evaporated to the crystallizing point.

The crystals of chloride of barium are flat, four-sided tables, colorless and transparent. They contain 2 equivalents of water, easily driven off by heat;—100 parts of water dissolve 43·5 parts at 60°, and 78 parts at 222°, which is the boiling-point of the saturated solution.

Nitrate of baryta. BaO, NO_5.—The nitrate is prepared by methods exactly similar to the above, nitric acid being substituted for the hydrochloric. It crystallizes in transparent colorless octahedrons, which are anhydrous. They require for solution 8 parts of cold, and 3 parts of boiling water. This salt is much less soluble in dilute nitric acid than in pure water; errors sometimes arise from such a precipitate of crystalline nitrate of baryta being mistaken for sulphate. It disappears on heating, or by large affusion of water.

Sulphate of baryta; heavy spar. BaO, SO_3.—Found native, often beautifully crystallized. This compound is always produced when sulphuric acid or a soluble sulphate is mixed with a solution of a barytic salt. It is not sensibly soluble in water or in any dilute acid, even nitric: hot oil of vitriol dissolves a little, but the greater part separates again on cooling. Sulphate of baryta is used as a pigment, but principally for the purpose of adulterating white lead; the native salt is ground to fine powder and washed with dilute sulphuric acid, by which its color is improved, and a little oxide of iron probably dissolved out. The specific gravity of the natural sulphate is as high as 4·4 to 4·8.

Sulphuret of barium. BaS.—The protosulphuret of barium is obtained in the manner already described; the higher sulphurets may be formed by boiling this compound with sulphur. Monosulphuret of barium crystallizes in thin and nearly colorless plates from a hot solution, which contain water, and are not very soluble; they are rapidly altered by the air. A strong solution of sulphuret may be employed in the preparation of hydrate of baryta, by boiling it with small successive portions of black oxide of copper, until a drop of the liquid ceases to precipitate a salt of lead black; the liquid being filtered, yields on cooling crystals of hydrate. In this reaction, besides hydrate of baryta, hyposulphite of that base, and subsulphuret of copper are produced; the latter is insoluble, and is removed by the filter, while most of the hyposulphite remains in the mother liquor.

Carbonate of baryta. BaO, CO_2.—The natural carbonate is called *Witherite;* the artificial is formed by precipitating the chloride or nitrate with an alkaline carbonate, or carbonate of ammonia. It is a heavy, white powder, very sparingly soluble in water, and chiefly useful in the preparation of the rarer barytic salts.

Solutions of hydrate and nitrate of baryta, and of chloride of barium are constantly kept in the laboratory as chemical tests, the first being employed to effect the separation of carbonic acid from certain gaseous mixtures, and the two latter to precipitate sulphuric acid from solution.

The soluble salts of baryta are poisonous, which is not the case with those of the base next to be described.

14

STRONTIUM.

The metal strontium may be obtained from its oxide by means similar to those described in the case of barium; it is white metal, heavy, oxidizable in the air, and capable of decomposing water at common temperatures.

The equivalent of strontium is 43·78, and its symbol is Sr.

PROTOXIDE OF STRONTIUM; STRONTIA. SrO.—This compound is best prepared by decomposing the nitrate by the aid of heat; it resembles in almost every particular the earth baryta, forming, like that substance, a white hydrate, soluble in water. A hot saturated solution deposits crystals on cooling which contain 12 equivalents of water. The hydrate has a great attraction for carbonic acid.

PEROXIDE OF STRONTIUM. SrO_2.—The peroxide is prepared in the same manner as peroxide of barium; it may be substituted for the latter in making peroxide of hydrogen.

The native carbonate and sulphate of strontia, met with in lead mines and other localities, serve for the preparation of the various salts by means exactly similar to those already described in the case of baryta; they have a very feeble degree of solubility in water.

CHLORIDE OF STRONTIUM. $SrCl$.—The chloride crystallizes in colorless needles or prisms, which are slightly deliquescent, and soluble in 2 parts of cold and still less of boiling water; they are also soluble in alcohol, and the solution, when kindled, burns with a crimson flame. The crystals contain 9 equivalents of water, which they lose by heat; at a higher temperature the chloride fuses.

NITRATE OF STRONTIA. SrO, NO_5.—This salt crystallizes in anhydrous octahedrons, which require for solution 5 parts of cold, and about half their weight of boiling water. It is principally of value to the pyrotechnist, who employs it in the composition of the well-known "red-fire."

CALCIUM.

This is a silver-white and extremely oxidable metal, obtained with great difficulty by means analogous to those by which barium and strontium are procured.

The equivalent of calcium is 20; its symbol is Ca.

PROTOXIDE OF CALCIUM; LIME. CaO.—This extremely important compound may be obtained in a state of considerable purity by heating to full redness for some time fragments of the black bituminous marble of Derbyshire or Kilkenny. If required absolutely pure, it must be made by igniting to whiteness, in a platinum crucible, an artificial carbonate of lime, procured by precipitating the nitrate by carbonate of ammonia. Lime in an impure state is prepared for building and agricultural purposes by calcining in a kiln, of suitable construction, the ordinary limestones which abound in many districts; a red heat, continued for some hours, is sufficient to disengage the whole of the carbonic acid. In the best contrived lime-kilns the process is carried on continuously, broken limestone and fuel being constantly thrown in at the top, and the burned lime raked out at intervals from beneath. Sometimes, when the limestones contain silica, and the heat has been very high, the lime refuses to slake, and is said to be *over-burned;* in this case a portion of silicate has been formed.

Pure lime is white, and often of considerable hardness; it is quite infusible, and phosphoresces, or emits a pale light at a high temperature. When moistened with water it slakes with great violence, evolving heat, and crumbling to a soft, white, bulky powder, which is a hydrate containing a single equivalent of water; the latter can be again expelled by a red heat. This hydrate

is soluble in water, but far less so than either the hydrate of baryta or of strontia, and what is very remarkable, the *colder* the water, the larger quantity of the compound is taken up. A pint of water at 60° dissolves about 11 grains, while at 212° only 7 grains are retained in solution. The hydrate has been obtained in thin delicate crystals by slow evaporation under the air-pump. Lime-water is always prepared for chemical and pharmaceutical purposes by agitating cold water with excess of hydrate of lime in a closely-stopped vessel, and then after subsidence, pouring off the clear liquid, and adding a fresh quantity of water, for another occasion,—there is not the least occasion for filtering the solution. Lime-water has a strong alkaline reaction, a nauseous taste, and when exposed to the air becomes almost instantly covered with a pellicle of carbonate, by absorption of carbonic acid from the atmosphere. It is used, like baryta-water, as a test for that substance, and also in medicine.

The hardening of mortars and cements is in a great measure due to the gradual absorption of carbonic acid; a very great length of time, however, usually elapses before this conversion into carbonate becomes complete. Mortar is known, under favorable circumstances, to acquire extreme hardness with age. Lime-cements which resist the action of water, contain oxide of iron, silica and alumina; they require to be carefully prepared and the stone not over-heated. When ground to powder and mixed with water, solidification speedily ensues, from causes not thoroughly understood, and the cement, once in this condition, is unaffected by wet. Parker's, or Roman cement, is made in this manner from the nodular masses of calcareo-argillaceous ironstone found in the London clay. Lime is of great importance in agriculture; it is found more or less in every fertile soil, and is often very advantageously added by the cultivator. The decay of vegetable fibre in the soil is promoted, and other important objects, as the destruction of certain hurtful compounds of iron in marsh and peatlands, is often attained.

Peroxide of calcium. CaO_2.—This is stated to resemble peroxide of barium, and to be obtainable by a similar process.

Chloride of calcium. $CaCl$.—Usually prepared by dissolving marble in hydrochloric acid; also a by-product in several chemical manufactures. The salt separates from a strong solution in colorless, prismatic, and exceedingly deliquescent crystals, which contain six equivalents of water. By heat, this water is expelled, and by a temperature of strong ignition the salt is fused. The crystals reduced to powder, are employed in the production of artificial cold by being mixed with snow or powdered ice, and the chloride strongly dried or in a fused condition is of great practical use in desiccating gases, for which purpose the latter are slowly transmitted through tubes filled with fragments of the salt. Chloride of calcium is also freely soluble in alcohol, which, when anhydrous, forms with it a definite crystallizable compound.

Sulphurets of calcium.—The simple sulphuret is obtained by reducing sulphate of lime at a high temperature by charcoal or hydrogen; it is nearly colorless, and but little soluble in water.—By boiling together hydrate of lime, water, and flowers of sulphur, a red solution is obtained, which on cooling deposits crystals of bi-sulphuret, which contain water. When the sulphur is in excess, and the boiling long-continued, a penta-sulphuret is generated; hyposulphuric acid is, as usual, formed in these reactions.

Sulphate of lime; gypsum; selenite. CaO, SO_3.—Native sulphate of lime in a crystalline condition, containing 2 equivalents of water, is found in considerable abundance in some localities; it is often associated with rock-salt. When regularly crystallized, it is termed *selenite*. Anhydrous sulphate of lime is also occasionally met with. The salt is formed by precipitation when a moderately concentrated solution of chloride of calcium is mixed with

sulphuric acid. Sulphate of lime is soluble in about 500 parts of cold water, and its solubility is a little increased by heat; the solution is precipitated by alcohol. Gypsum, or native hydrated sulphate, is largely employed for the purpose of making casts of statues and medals, and also for moulds in the porcelain and earthenware manufactures, and other applications. It is exposed to heat in an oven where the temperature does not exceed 260°, by which the water of crystallization is expelled, and afterwards reduced to fine powder. When mixed with water, it solidifies after a short time from the re-formation of the same hydrate; but this effect does not happen if the gypsum has been over-heated; it is often called plaster of Paris. Artificial colored marbles, or *scagliola*, are frequently prepared by inserting pieces of natural stone in a soft stucco containing this substance, and polishing the surface when the cement has become hard. Sulphate of lime is one of the most common impurities of spring water.

Carbonate of lime; chalk; limestone; marble. CaO, CO_2.—Carbonate of lime, often more or less contaminated by oxide of iron, clay and organic matter, forms rocky beds, of immense extent and thickness, in almost every part of the world. These present the greatest diversities of texture and appearance, arising, in a great measure, from changes to which they have been subjected since their deposition. The most ancient and highly crystalline limestones are destitute of visible organic remains, while those of more recent origin are often entirely made up of the shelly exuviæ of once living beings. Sometimes these latter are of such a nature as to show that the animals inhabited fresh water; marine species and corals are, however, most abundant. Cavities in limestone, and other rocks, are very often lined with magnificent crystals of carbonate of lime or calcareous spar, which have evidently been slowly deposited from a watery solution. Carbonate of lime is always precipitated when an alkaline carbonate is mixed with a solution of that base.

Although this substance is not sensibly soluble in pure water, it is freely taken up when carbonic acid happens at the same time to be present. If a little lime-water be poured into a vessel of that gas, the turbidity first produced disappears on agitation, and a transparent solution of carbonate of lime in excess of carbonic acid is obtained. This solution is decomposed completely by boiling, the carbonic acid being expelled, and the carbonate precipitated. Since all natural waters contain dissolved carbonic acid, it is to be expected that lime in this condition should be of very common occurrence; and such is really found to be the fact, river, and more especially spring water, almost invariably containing carbonate of lime thus dissolved. In limestone districts, this is often the case to a great extent. Boilers in which such water is heated, speedily become lined with a thick stony incrustation, which is often a source of great inconvenience. The beautiful stalactitic incrustations of limestone caverns, and the deposits of calc-sinter or travertin upon various objects, and upon the ground in many places, are thus explained.

Crystallized carbonate of lime exhibits the curious property of dimorphism; calcareous spar and arragonite, although possessing the same chemical composition, both containing single equivalents of lime and carbonic acid, and nothing besides, have different crystalline forms, different densities, and different optical properties.

The former occurs very abundantly in crystals derived from an obtuse rhomboid, whose angles measure 105° 5′ and 74° 55′; its density varies from 2·5 to 2·8. The rarer variety, or arragonite, is found in crystals whose primary form is a right rhombic prism; a figure having no geometrical relation to the preceding; it is, besides, heavier and harder.

Phosphates of lime.—A number of distinct compounds of lime and phosphoric acid probably exist. Two *tribasic phosphates*, $2CaO, HO, PO_5$ and $3CaO$,

PO_5, are produced where the corresponding soda-salts are added in solution to chloride of calcium; the first is slightly crystalline, and the second gelatinous. When the first phosphate is digested with ammonia, or dissolved in acid and re-precipitated by that alkali, it is converted into the second. The earth of bones consists principally of what appears to be a combination of these two salts. Another phosphate, containing 2 equivalents of basic water, has been described, which completes the series; it is formed by dissolving either of the preceding in phosphoric, hydrochloric, or nitric acid, and evaporating until the salt separates on cooling in small platy crystals. It is this substance which yields phosphorus, when heated with charcoal in the ordinary process of manufacture, before described. *Bibasic* and *monobasic phosphates of lime* also exist. These phosphates, although insoluble in water, dissolve readily in dilute acids, even acetic acid.

FLUORIDE OF CALCIUM; FLUOR-SPAR. CaF.—This substance is important as the most abundant natural source of hydrofluoric acid and the other fluorides. It occurs beautifully crystallized, in various colors, in lead-veins, the crystals having commonly the cubic, but sometimes the octahedral form, parallel to the faces of which latter figure they always cleave. Some varieties, when heated, emit a greenish phosphorescent light. The fluoride is quite insoluble in water, and is decomposed by oil of vitriol in the manner already mentioned.*

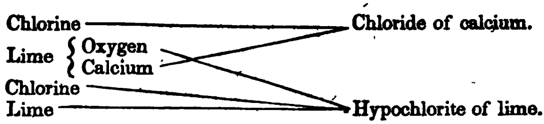
CHLORIDE OF LIME; BLEACHING POWDER.—When hydrate of lime, very slightly moist, is exposed to chlorine gas, the latter is eagerly absorbed, and a compound produced which has attracted a great deal of attention; this is the bleaching powder of commerce, now manufactured on an immense scale, for bleaching linen and cotton goods. It is requisite, in preparing this substance, to avoid with the greatest care all elevation of temperature, which may be easily done by slowly supplying the chlorine in the first instance. The product, when freshly and well prepared, is a soft, white powder, which attracts moisture from the air, and exhales an odor sensibly different from that of chlorine. It is soluble in about 10 parts of water, merely the unaltered hydrate being left behind; the solution is highly alkaline, and bleaches feebly. When hydrate of lime is suspended in cold water, and chlorine gas transmitted through the mixture, the lime is gradually dissolved, and the same peculiar bleaching compound produced; the alkalis also, either caustic or carbonated, may, by similar means, be made to absorb a large quantity of chlorine, and give rise to corresponding compounds; such are the "disinfecting solutions" of M. Labarraque.

The most consistent view of the constitution of these curious compounds is that which supposes them to contain salts of hypochlorous acid, a substance as remarkable for bleaching powers as chlorine itself; and this opinion seems borne out by a careful comparison of the properties of the bleaching salts with those of the true hypocholorites. Hypochlorous acid can be actually obtained from good bleaching powder, by distilling it with dilute sulphuric or nitric acid, in quantity insufficient to decompose the whole; when the acid is used in excess, chlorine is disengaged.†

If this view be correct, chloride of calcium must be formed simultaneously with the hypochlorite, as in the following diagram—

* Fluoride of calcium exists in the enamel of the teeth, and is also a constituent of fossil bones, and very probably of recent bone, the presence of organic matter rendering its detection difficult.—R. B.

† M. Gay-Lussac, Ann. Chim. et Phys., 3d Series, v. p. 296.



When the temperature of the hydrate of lime has risen during the absorption of the chlorine, or when the compound has been subsequently exposed to heat, its bleaching properties are impaired or altogether destroyed; it then contains chlorate of lime and chloride of calcium; oxygen, in variable quantity, is usually set free. The same change seems to ensue by long keeping, even at the common temperature of the air. In an open vessel it is speedily destroyed by the carbonic acid of the atmosphere. Commercial bleaching-powder thus constantly varies in value with its age, and with the care originally bestowed upon its preparation; the best may contain about 30 per cent. of available chlorine, easily liberated by an acid, which is, however, far short of the theoretical quantity.

The general method in which this substance is employed for bleaching is the following:—the goods are first immersed in a dilute solution of chloride of lime and then transferred to a vat containing dilute sulphuric acid; the chlorine or hypochlorous acid thus disengaged in contact with the cloth, causes the destruction of the coloring matter. This process is often repeated, it being unsafe to use strong solutions. White patterns are on this principle imprinted upon colored cloth, the figures being stamped with tartaric acid thickened with gum-water, and then the stuff immersed in the chloride bath, when the parts to which no acid has been applied, remain unaltered, while the printed portions are bleached.

For purifying an offensive or infectious atmosphere, *as an aid to proper ventilation*, the bleaching powder is very convenient. The solution is exposed in shallow vessels, or cloths steeped in it are suspended in the apartment, when the carbonic acid of the air slowly decomposes the chloride. An addition of a strong acid causes rapid disengagement of chlorine.

The value of any sample of bleaching-powder may be easily determined by the following method, in which the loosely-combined chlorine is estimated by its effect in peroxidizing a proto-salt of iron, of which two equivalents require one of chlorine; the latter acts by decomposing water and liberating a corresponding quantity of oxygen—78 grains of green sulphate of iron are dissolved in about two ounces of water and acidulated by a few drops of sulphuric or hydrochloric acid; this quantity will require for peroxidation exactly 10 grains of chlorine. Fifty grains of the chloride of lime to be examined are next rubbed up with a little tepid water, and the whole transferred to the alkalimeter before described, which is then filled up to 0 with water, after which the contents are well mixed by agitation. The liquid is next gradually poured into the solution of iron, with constant stirring until the latter has become peroxidized, which may be known by a drop ceasing to give a deep blue precipitate with red ferrocyanide of potassium. The number of grain-measures of the chloride solution employed may then be read off, and since these must contain 10 grains of serviceable chlorine, the quantity of the latter in the 50 grains may be easily reckoned. Thus, suppose 72 such measures have been taken, then

Measures.		Grns. chlorine.		Measures.		Grns. chlorine.
72	:	10	: :	100	:	13·89

The bleaching-powder contains therefore, 27·78 per cent.*

* Graham, Elements, p. 353.

Baryta, strontia, and lime, are thus distinguished from all other substances, and from each other.

Caustic potash, when free from carbonate, and caustic ammonia, occasions no precipitates in dilute solutions of the earths, especially of the first two, the hydrates being soluble in water.

Alkaline carbonates, and carbonate of ammonia, give white precipitates, insoluble in excess of the precipitant, with all three.

Sulphuric acid, or a sulphate, added to very dilute solutions of the earths in question, gives an immediate white precipitate with baryta, a similar precipitate after a short interval with strontia, and occasions no change with the lime-salt. The precipitates with baryta and strontia are quite insoluble in nitric acid.

Solution of sulphate of lime gives an instantaneous cloud with baryta, and one with strontia after a little time. Sulphate of strontia is itself sufficiently soluble to occasion turbidity when mixed with chloride of barium.

Lastly, the soluble oxalates give a white precipitate in the most dilute solutions of lime, which is not dissolved by a drop or two of hydrochloric acid. This is an exceedingly characteristic test.

The chlorides of strontium and calcium dissolved in alcohol color the flame of the latter red or purple; salts of baryta communicate to flame a pale green tint.

MAGNESIUM.

A few pellets of sodium are placed at the bottom of a test-tube of hard German glass, and covered with fragments of fused chloride of magnesium. The heat of a spirit-lamp is then applied until reaction has been induced: this takes place with great violence and elevation of temperature, chloride of sodium being formed, and metallic magnesium set free. When the tube and its contents are completely cold, it is broken up, and the fragments put into cold water, by which the metal is separated from the salt.

Magnesium is a white, malleable metal, fusible at a red heat, and not sensibly acted upon by cold water; heated in the air, it burns and produces magnesia, which is the only oxide. Sulphuric and hydrochloric acids dissolve it readily, evolving hydrogen.

The equivalent of this metal is 12·67, and its symbol Mg.

MAGNESIA; CALCINED MAGNESIA. MgO.—This is prepared with great ease by exposing the *magnesia alba* of pharmacy to a full red heat in an earthen or platinum crucible. It forms a soft, white powder, which slowly attracts moisture and carbonic acid from the air, and unites quietly with water to a hydrate which possesses a feeble degree of solubility, requiring about 5000 parts of water at 60° and 36,000 parts at 212°. The alkalinity of magnesia can only be observed by placing a small portion in a moistened state upon test-paper; it neutralizes acids, however, in the most complete manner. It is infusible.

CHLORIDE OF MAGNESIUM. MgCl.—When magnesia, or its carbonate, is dissolved in hydrochloric acid, there can be no doubt respecting the simultaneous production of chloride of magnesium and water; but when this solution comes to be evaporated to dryness, the last portions of water are retained with such obstinacy, that decomposition of the water is brought about by the concurring attractions of magnesium for oxygen, and of chlorine for hydrogen; hydrochloric acid is expelled, and magnesia remains. If, however, sal-ammoniac, or chloride of potassium happen to be present, a double salt is produced, which is easily rendered anhydrous. The best mode of preparing the chloride is to divide a quantity of hydrochloric acid into two equal portions, to

neutralize one with magnesia, and the other with ammonia, or carbonate of ammonia; to mix these solutions, evaporate them to dryness, and then expose the salt to a red heat in a loosely-covered porcelain crucible. Sal-ammoniac sublimes, and chloride of magnesium in a fused state remains; the latter is poured out upon a clean stone, and when cold, transferred to a well-stopped bottle.

The chloride so obtained is white and crystalline. It is very deliquescent and highly soluble in water, from which it cannot again be recovered by evaporation, for the reasons just mentioned. When long exposed to the air in a melted state, it is converted into magnesia. It is soluble in alcohol.

Sulphate of magnesia; Epsom salt. MgO, SO_3+7HO.—This salt occurs in sea-water, and in that of many mineral springs, and is now manufactured in large quantities by acting on magnesian lime-stone by diluted sulphuric acid, and separating the sulphate of magnesia from the greater part of the slightly-soluble sulphate of lime by the filter. The crystals are derived from a right rhombic prism; they are soluble in an equal weight of water at 60°, and in a still smaller quantity at 212°. The salt has a nauseous bitter taste, and like many other neutral salts, purgative properties. When exposed to heat, 6 equivalents of water readily pass off, the seventh being energetically retained. Sulphate of magnesia forms beautiful double salts with the sulphates of potash and ammonia, which contain 6 equivalents of water of crystallization.

Carbonate of magnesia.—The *neutral carbonate*, MgO, CO_2, occurs native in rhombohedral crystals, resembling those of calcareous spar, imbedded in talc-slate; a soft earthy variety is sometimes met with.

When magnesia alba is dissolved in carbonic acid water, and the solution left to evaporate spontaneously, small prismatic crystals are deposited, which consist of carbonate of magnesia, with three equivalents of water.

The *magnesia alba* itself, although often called carbonate of magnesia, is not so in reality; it is a compound of carbonate with hydrate. It is prepared by mixing hot solutions of carbonate of potash or soda, and sulphate of magnesia, the latter being kept in slight excess, boiling the whole a few minutes, during which time much carbonic acid is disengaged, and then well washing the precipitate so produced. If the solution be very dilute, the magnesia alba is exceedingly light and bulky; if otherwise, it is denser, but its composition does not sensibly vary. It contains in 100 parts

Magnesia	41·6
Carbonic acid	36·0
Water	22·4
	100

Or, 5 eq. magnesia, 4 eq. carbonic acid, and 6 eq. water.

Magnesia alba is slightly soluble in water, especially when cold.

Phosphate of magnesia. $2MgO, HO, PO_5+14HO$.—This salt separates in small colorless prismatic crystals when solutions of phosphate of soda and sulphate of magnesia are mixed and suffered to stand some time. Mr. Graham states, that it is soluble in about 1000 parts of cold water, but Berzelius describes a phosphate which only requires 15 parts of water for solution: this can hardly be the same substance. Phosphate of magnesia exists in the grain of the cereals, and can be detected in considerable quantity in beer.

Phosphate of magnesia and ammonia. $2MgO, NH_4O, PO_5+12HO$.—When a soluble phosphate is mixed with salt of magnesia, and ammonia or its carbonate added, a crystalline precipitate, having the above composition,

subsides, immediately, if the solutions are concentrated, and after some time if very dilute; in the latter case, the precipitation is promoted by stirring. This salt is slightly soluble in pure water, but scarcely so in saline liquids. When heated, it is resolved into bibasic phosphate of magnesia, containing 36·68 per cent. of magnesia. At a strong red heat it fuses to a white enamel-like mass. The phosphate of magnesia and ammonia sometimes forms a urinary calculus.

In practical analysis, magnesia is often separated from solutions by bringing it into this state. The liquid, free from lime, alumina, &c., is mixed with phosphate of soda and excess of ammonia, and gently heated for a short time. The precipitate is collected upon a filter and thoroughly washed with water containing a little sal-ammoniac, after which it is dried, ignited to redness, and weighed. The proportion of magnesia is then easily calculated.

SILICATES OF MAGNESIA.—The following natural compounds belong to this class:—*Steatite*, or *soap-stone*, MgO, SiO_3, a soft, white, or pale-colored, amorphous substance, found in Cornwall and elsewhere;—*Meerschaum*, MgO, SiO_3+HO, from which pipe-bowls are often manufactured;—*Chrysolite*, $3MgO, SiO_3$, a crystallized mineral, sometimes employed for ornamental purposes. A portion of magnesia is commonly replaced by protoxide of iron, which communicates a green color. *Serpentine* is a combination of silicate and hydrate of magnesia;—*Jade*, an exceedingly hard stone, brought from New Zealand, contains silicate of magnesia combined with silicate of alumina; its green color is due to oxide of chromium;—*Augite* and *hornblende* are essentially double salts of silicic acid, magnesia, and lime, in which the magnesia is more or less replaced by its isomorphous substitute, protoxide of iron.

The salts of magnesia are strictly isomorphous with those of oxide of zinc, protoxide of iron, oxide of copper, &c.; they are usually colorless, and are easily recognized by the following characters:—

A gelatinous white precipitate with caustic alkalis, including ammonia, insoluble in excess, but soluble in solution of sal-ammoniac.

A white precipitate with the carbonates of potash and soda, but *none* with carb. ammonia in the cold.

A white crystalline precipitate with soluble phosphates, on the addition of a little ammonia.

SECTION III.

METALS OF THE EARTHS PROPER.

ALUMINUM OR ALUMINIUM.

ALUMINA, the only known oxide of this metal, is a substance of very abundant occurrence in nature in the state of silicate, as in felspar and its associated minerals, and in the various modifications of clay thence derived. Aluminium is prepared in the same manner as magnesium, but with rather more difficulty; a platinum or porcelain crucible must be used, the cover of which is bound down by a wire. The metal, separated by cold water from the alkaline chloride, has a gray color and perfect lustre. It is fusible with great difficulty, and when heated in the air or in oxygen, takes fire and burns with brilliancy, producing alumina.

Aluminium has for its equivalent the number 13·69; its symbol is Al.

ALUMINA. Al_2O_3.—This substance is inferred to be a sesquioxide, from its isomorphism with the red oxide of iron. It is prepared by mixing solution of alum with excess of ammonia, by which an extremely bulky, white, gelatinous precipitate of hydrate of alumina is thrown down. This is washed, dried, and ignited to whiteness. Thus obtained, alumina constitutes a white, tasteless, coherent mass, very little acted upon by acids. The hydrate, on the contrary, when simply dried in the air, or by gentle heat, dissolves freely in dilute acid, and in caustic potash or soda, from which it is precipitated by the addition of sal-ammoniac. Alumina is fusible before the oxy-hydrogen blow-pipe. The mineral called *corundum*, of which the ruby and sapphire are transparent varieties, consists of nearly pure alumina in a crystallized state, with a little coloring oxide; emery, used for polishing glass and metals, is a coarse variety of corundum. Alumina is a very feeble base, and its salts have often an acid reaction.

CHLORIDE OF ALUMINIUM. Al_2Cl_3.—The solution of alumina in hydrochloric acid behaves, when evaporated to dryness, like that of magnesia, the chloride being decomposed by the water, and alumina and hydrochloric acid produced. The chloride may be thus prepared:—Pure precipitated alumina is dried and mixed with lamp black, and the mixture strongly calcined in a covered crucible. It is then transferred to a porcelain tube fixed across a furnace, and heated to redness in a stream of chlorine gas, when the alumina, yielding to the attraction of the chlorine on the one hand, and the carbon on the other, for each of its constituents, suffers decomposition, carbonic oxide being disengaged, and chloride of aluminium formed; the latter sublimes, and condenses in the cool part of the tube.

Chloride of aluminium is a crystalline yellowish substance, excessively greedy of moisture, and very soluble. Once dissolved, it cannot be again recovered. It is said to combine with sulphuretted and phosphuretted hydrogen, and with ammonia.

SULPHATE OF ALUMINA. $Al_2O_3, 3SO_3+18HO$.—Prepared by saturating dilute sulphuric acid with hydrate of alumina, and evaporating. It crystallizes in thin, pearly plates, soluble in 2 parts of water; it has a sweet and astringent taste, and an acid reaction. Heated to redness, it is decomposed,

leaving pure alumina. Two other sulphates of alumina, with excess of base, are also described, one of which is insoluble in water.

Sulphate of alumina combines with the sulphates of potash, soda and ammonia forming double salts of great interest, the *alums*. Common alum, the source of all the preparations of alumina, contains Al_2O_3, $3SO_3$+KO, SO_3+24HO. It is manufactured, on a very large scale, from a kind of slaty clay, loaded with bisulphuret of iron, which abounds in certain parts. This is gently roasted, and then exposed to the air in a moistened state: oxygen is absorbed, the sulphur becomes acidified, sulphate of protoxide of iron, and sulphate of alumina are produced, and afterwards separated by lixiviation with water. The solution is next concentrated, and mixed with a quantity of chloride of potassium, which decomposes the iron-salt, forming protochloride of iron and sulphate of potash, which latter combines, with the sulphate of alumina, to alum. By crystallization, the alum is separated from the highly-soluble chloride of iron, and afterwards easily purified by a repetition of that process. Other methods of alum-making exist, and are sometimes employed. Potash alum crystallizes in colorless, transparent octahedrons, which often exhibit the faces of the cube. It has a sweetish and astringent taste, reddens litmus paper, and dissolves in 18 parts of water at 60°, and in its own weight of boiling water. Exposed to heat, it is easily rendered anhydrous, and, by a very high temperature, decomposed. The crystals have little tendency to change in the air. Alum is largely used in the arts, in preparing skins, dyeing, &c.; it is occasionally contaminated with oxide of iron, which interferes with some of its applications. The celebrated Roman alum, made from *alum-stone*, a felspathic rock, altered by sulphurous vapors, was once much prized on account of its freedom from this impurity.

A mixture of dried alum and sugar, carbonized in an open pan, and then heated to redness, out of contact of air, furnishes the *pyrophorus of Homberg*, which ignites spontaneously on exposure to the atmosphere. The essential ingredient is, in all probability, finely-divided sulphuret of potassium.

Soda-alum, in which sulphate of soda replaces sulphate of potash, has a form and constitution similar to that of the salt described; it is, however, much more soluble, and difficult to crystallize.

Ammonia-alum, containing NH_4O, SO_3, instead of KO, SO_3, very closely resembles common potash-alum, having the same figure, and appearance, and constitution, and nearly the same degree of solubility as that substance. It is sometimes manufactured for commercial use. When heated to redness, it yields pure alumina.

Few of the other salts of alumina, except the silicates, present points of interest; these latter are of great importance. Silicates of alumina enter into the composition of a number of crystallized minerals, among which felspar occupies, by reason of its abundant occurrence, a prominent place. Granite, porphyry, trachyte, and other ancient unstratified rocks, consist in great part of this mineral, which, under peculiar circumstances, by no means well understood, suffers complete decomposition, becoming converted into a soft, friable mass of earthy matter. This is the origin of clay; the change itself is seen in great perfection in certain districts of Devonshire and Cornwall, the felspar of the fine white granite of those localities being often disintegrated to an extraordinary depth, and the rock altered to a substance resembling soft mortar. By washing this, finely-divided matter is separated from the quartz and mica, and the milk-like liquid being collected in tanks and suffered to stand, deposits the suspended clay, which is afterwards dried, first in the air and afterwards in a stove, and employed in the manufacture of porcelain. The composition assigned to unaltered felspar is Al_2O_3, $3SiO_3$+KO, SiO_3, or alum,

having silicic acid in the place of sulphuric. The exact nature of the change by which it passes into porcelain clay is unknown, although it evidently consists in the abstraction of silica and alkali.*

When the decomposing rock contains oxide of iron, the clay produced is colored. The different varieties of shale and slate result from the alteration of ancient clay-beds, apparently in many instances by the infiltration of water holding silica in solution; the dark appearance of some of these deposits is due to bituminous matter.

It is a common mistake to confound clay with alumina; all clays are essentially silicates of that base; they often vary a good deal in composition. Dilute acids exert little action on these bodies; but by boiling with oil of vitriol, alumina is dissolved out, and finely-divided silica left behind. Clays containing an admixture of carbonate of lime are termed *marls*, and are recognized by effervescing with acids.

A basic silicate of alumina, $2Al_2O_3, SiO_3$, is found crystallized, constituting the beautiful mineral called *cyanite*. The compounds formed by the union of the silicates of alumina with other silicates, are almost innumerable, a soda-felspar, *albite*, containing that alkali in place of potash, is known, and there are two somewhat similar lithia-compounds, *spodumene* and *petalite*. The *zeolites* belong to this class: *analcime*, *nepheline*, *mesotype*, &c., are double silicates of soda and alumina, with water of crystallization. *Stilbite*, *heulandite*, *laumonite*, *prehnite*, &c. &c., consist of silicate of lime, combined with silicate of alumina. The *garnets*, *axinite*, *mica*, &c., have a similar composition, but are anhydrous. Peroxide of iron is very often substituted for alumina in these minerals.

Alumina, when in solution, is distinguished without difficulty.

Caustic potash and soda occasion white gelatinous precipitates of hydrate of alumina, freely soluble in excess of the alkali.

Ammonia produces a similar precipitate, insoluble in excess of the re-agent.

The alkaline carbonates, and carbonate of ammonia precipitate the hydrate, with escape of carbonic acid, no carbonate being known. The precipitates are insoluble in excess.

GLUCINUM.

This metal is prepared from the chloride in the same manner as aluminium. It is fusible with great difficulty, not acted upon by cold water, and burns when heated in the air, producing glucina.

The equivalent of glucinum is 26·5, and the symbol G.

GLUCINA, G_2O_3, is a rare earth found in the *emerald*, *beryl*, *and euclase*, from which it may be extracted by a process of tolerable simplicity. It very much resembles alumina, but is distinguished from that substance by its solubility, when freshly precipitated, in a cold solution of carbonate of ammonia, from which it is again thrown down on boiling. The salts of glucina have a sweet taste: whence its name (γλυκυς).

* A specimen of white porcelain-clay from Dartmoor, Devon, gave the author the following result on analysis:—

Silica	47·20
Alumina, with trace of iron and manganese	38·80
Lime	·24
Water	12·
Alkali and loss	1·76
	100·

YTTRIUM.

The metal of a very rare earth, *yttria*, contained in a few scarce minerals. The name is derived from Ytterby, a place in Sweden, where one of these, *gadolinite*, is found. It is obtained from the chloride by the process already described; it resembles in character the preceding metal.

The equivalent of Yttrium is 32·2; its symbol is Y.

YTTRIA, YO, has properties from which it is distinguished from the other earths; some of its salts are said to have a red or purplish tint.*

ZIRCONIUM.

Prepared by heating the double fluoride of zirconium and potassium with potassium, and separating the salt with cold water. The metal is black, and acquires a feeble lustre when burnished. It takes fire when heated in the air.

The equivalent of zirconium is 33·62, and its symbol, Zr.

ZIRCONIA, Zr_2O_3, is a rare earth, very closely resembling alumina, found in the mineral *zircon*; the salts are colorless and have an astringent taste.

THORIUM.

The metal of an earth from a very rare mineral, *thorite*; it agrees in character with aluminium, and is obtained by similar means.

The equivalent of thorium is 59·59, and its symbol Th.

THORINA, ThO, is remarkable for its great specific gravity, and is otherwise distinguished by peculiar properties which separate it from all other substances.

Manufacture of Glass, Porcelain, and Earthenware.

GLASS.—Glass is a mixture of various insoluble silicates, with excess of silica, altogether destitute of crystalline structure; the simple silicates, formed by fusing the bases with silicic acid in equivalent proportions, very often crystallize, which happens also with the greater number of the natural silicates included among the earthy minerals. Compounds identical with some of these are also occasionally formed in artificial processes, where large masses of melted glassy matter are suffered to cool slowly. The alkaline silicates, when in a state of fusion, have the power of dissolving a large quantity of silica.

Two principal varieties of glass are met with in commerce, namely, glass composed of silica, alkali, and lime, and glass containing a large proportion of silicate of lead; *crown* and *plate-glass* belong to the former division; *flint-glass*, and the material of artificial gems to the second. The lead promotes fusibility, and confers also density and lustre. Common green bottle glass contains no lead, but much silicate of black oxide of iron, derived from the impure materials. The principle of the glass manufacture is very simple. Silica, in the shape of sand, is heated with carbonate of potash or soda, and slaked lime or oxide of lead; at a high temperature, fusion and combination occur, and the carbonic acid is expelled. When the melted mass has become perfectly clear and free from air-bubbles, it is left to cool until it assumes the peculiar tenacious condition proper for working.

* According to Professor Mosander, the substance hitherto called yttria is in reality a mixture of the oxides of three different metals, possessing different properties, viz., *yttrium*, properly so called, and two new metals, termed *erbium* and *terbium*.—Phil. Mag., October, 1843.

The operation of fusion is conducted in large crucibles of refractory fire-clay, which in the case of lead-glass, are covered by a dome at the top, and have an opening at the side by which the materials are introduced and the melted glass withdrawn. Great care is exercised in the choice of the sand, which must be quite white and free from oxide of iron. Red-lead, one of the higher oxides, is preferred to litharge, although immediately reduced to prot-oxide by the heat, the liberated oxygen serving to destroy any combustible matter which might accidentally find its way into the crucible and stain the glass by reducing a portion of the lead. Potash gives a better glass than soda, although the latter is very generally employed, from its lower price. A certain proportion of broken and waste glass of the same kind is always added to the other materials.

Articles of blown glass are thus made:—The workman begins by collecting a proper quantity of soft, pasty glass at the end of his *blow-pipe*, an iron tube, five or six feet in length, terminated by a mouth-piece of wood; he then commences blowing, by which the lump is expanded into a kind of flask, susceptible of having its form modified by the position in which it is held, and the velocity of rotation continually given to the iron tube. If an open-mouthed vessel is to be made, an iron rod called a *pontil* or *puntil* is dipped into the glass-pot and applied to the bottom of the flask, to which it thus serves as a handle, the blow-pipe being removed by the application of a cold iron to the neck. The vessel is then re-heated at a hole left for the purpose in the wall of the furnace, and the aperture enlarged, and the vessel otherwise altered in figure by the aid of a few simple tools, until completed. It is then detached, and carried to the annealing oven, where it undergoes slow and gradual cooling during many hours, the object of which is to obviate the excessive brittleness always exhibited by glass which has been quickly cooled. The large circular *tables* of crown-glass are made by a very curious process of this kind; the globular flask at first produced, transferred from the blow-pipe to the pontil, is suddenly made to assume the form of a flat disc by the centrifugal force of the rapid rotatory movement given to the rod. Plate-glass is cast upon a flat metal table, and after very careful annealing, ground true and polished by suitable machinery. Tubes are made by rapidly drawing out a hollow cylinder; and from these a great variety of useful small apparatus may be constructed with the help of a lamp and blow-pipe, or still better, the bellows-table of the barometer-maker. Small tubes may be bent in the flame of a spirit-lamp or gas-jet, and cut with great ease by a file, a scratch being made, and the two portions pulled or broken asunder in a way easily learned by a few trials.

Specimens of the two chief varieties of glass gave the following results on analysis:

Bohemian plate glass (excellent).*		English flint glass.†	
Silica	60	Silica	51·93
Potash	25	Potash	13·77
Lime	12·5	Oxide of lead	33·28
	97·5		98·98

Different colors are often communicated to glass by metallic oxides. Thus oxide of cobalt gives deep blue; oxide of manganese, amethyst; sub-oxide of copper, ruby-red; black oxide of copper, green; the oxides of iron, dull green or brown, &c. These are either added to the melted contents of the glass-

* Mitscherlich, Lehrbuch, ii. p. 167.
† Faraday, quoted by Turner, Elements, p. 516.

pot, in which they dissolve, or applied in a particular manner to the surface of the plate or other object, which is then re-heated until fusion of the coloring matter occurs; such is the practice of enameling, and glass-painting. An opaque white appearance is given by oxide of tin;—the enamel of watch-faces is thus prepared.

When silica is melted with twice its weight of carbonate of potash or soda, and the product treated with water, the greater part dissolves, yielding a solution from which acids precipitate gelatinous silica. This is the *soluble glass* sometimes mentioned by chemical writers; its solution has been used for rendering muslin and other fabrics of cotton or linen less combustible.

Porcelain and earthenware.—The plasticity of natural clays, and their hardening when exposed to heat, are properties which suggested in very early times their application to the making of vessels for the various purposes of daily life; there are few branches of industry of higher antiquity than that exercised by the potter.

True porcelain is distinguished from earthenware by very obvious characters. In porcelain the *body* of the ware is very compact and translucent, and breaks with a conchoidal fracture, symptomatic of a commencement of fusion. The glaze, too, applied for giving a perfectly smooth surface, is closely adherent, and in fact graduates by insensible degrees into the substance of the body. In earthenware, on the contrary, the fracture is open and earthy, and the glaze detachable with greater or less facility. The compact and partly glassy character of porcelain is the result of the admixture with the clay of a small portion of some substance, fusible at the temperature to which the ware is exposed when baked or fired, and which, absorbed by the more infusible portion, binds the whole into a solid mass on cooling; such substances are found in felspar, and in a small admixture of silicate of lime, or alkali. The clay employed in porcelain-making is always directly derived from decomposed felspar, none of the clays of the secondary strata being pure enough for the purpose; it must be white, and free from oxide of iron. To diminish the retraction which this substance undergoes in the fire, a quantity of finely-divided silica, carefully prepared by crushing and grinding calcined flints or chert, is added, together with a proper proportion of felspar or other fusible material, also reduced to impalpable powder. The utmost pains are taken to effect perfect uniformity of mixture, and to avoid the introduction of particles of grit or other foreign bodies. The ware itself is fashioned either on the potter's wheel;—a kind of vertical lathe;—or in moulds of plaster of Paris, and dried, first in the air, afterwards by artificial heat, and at length completely hardened by exposure to the temperature of ignition. The porous *biscuit* is now fit to receive its glaze, which may be either ground felspar, or a mixture of gypsum, silica, and a little porcelain clay, diffused through water. The piece is dipped for a moment into this mixture, and withdrawn; the water sinks into its substance, and the powder remains evenly spread upon its surface; it is once more dried, and lastly, fired at an extremely high temperature.

The porcelain-furnace is a circular structure of masonry, having several fire-places, and surmounted by a lofty dome. Dry wood or coal is consumed as fuel, and its flame directed into the interior, and made to circulate around and among the earthen cases, or *seggars*, in which the articles to be fired are packed. Many hours are required for this operation, which requires very careful management. After the lapse of several days, when the furnace has completely cooled, the contents are removed in a finished state, so far as regards the ware.

The ornamental part, consisting of gilding and paintings in enamel, has yet

to be executed, after which the pieces are again heated, in order to flux the colors. This operation has sometimes to be repeated more than once.

The manufacture of porcelain in Europe is of modern origin; the Chinese have possessed the art from the commencement of the seventh century, and their ware is, in some respects, altogether unequaled. The materials employed by them are known to be *kaolin* or decomposed felspar; *petuntze*, or quartz reduced to fine powder; and the ashes of fern, which contain carbonate of potash.

STONEWARE.—This is a coarse kind of porcelain, made from clay containing oxide of iron and a little lime, to which it owes its partial fusibility. The glazing is performed by throwing common salt into the heated furnace; this is volatilized, and decomposed by the joint agency of the silica of the ware, and of vapor of water always present; hydrochloric acid and soda are produced, the latter forming a silicate, which fuses over the surface of the ware, and gives a thin, but excellent glaze.

EARTHENWARE.—The finest kind of earthenware is made from a white secondary clay, mixed with a considerable quantity of silica. The articles are thoroughly dried and fired, after which they are dipped into a readily fusible glaze-mixture, of which oxide of lead is usually an important ingredient, and, when dry, re-heated to the point of fusion of the latter. The whole process is much easier of execution than the making of porcelain, and demands less care. The ornamental designs in blue and other colors so common upon plates and household articles, are printed upon paper in enamel pigment, mixed with oil, and transferred, while still wet, to the unglazed ware. When the ink becomes dry, the paper is washed off, and the glazing completed.

The coarser kinds of earthenware are sometimes covered with a whitish opaque glaze, which contains the oxides of lead and tin; such glaze is very liable to be attacked by acids, and is dangerous for culinary vessels.

Crucibles, when of good quality, are very valuable to the practical chemist. They are made of clay free from lime, mixed with sand or ground ware of the same description. The Hessian and Cornish crucibles are among the best. Sometimes a mixture of plumbago and clay is employed for the same purpose, and powdered coke has been also used with the earth: such crucibles bear rapid changes of temperature with impunity.

SECTION IV.

OXIDABLE METALS PROPER, WHOSE OXIDES FORM POWERFUL BASES.

MANGANESE.

MANGANESE is tolerably abundant in nature in an oxidized state, forming or entering into the composition of, several interesting minerals. Traces of this substance are very frequently found in the ashes of plants.

Metallic manganese, or perhaps strictly, carburet of manganese, may be best prepared by the following process. The carbonate is calcined in an open vessel, by which it becomes converted into a dense brown powder; this is intimately mixed with a little charcoal, and about one-tenth of its weight of anhydrous borax. A charcoal crucible is next prepared by filling a Hessian or Cornish crucible with moist charcoal powder, introduced a little at a time, and rammed as hard as possible. A smooth cavity is then scooped in the centre, into which the above-mentioned mixture is compressed, and covered with charcoal-powder. The lid of the crucible is luted down with a little fire-clay, and the whole arranged in a very powerful wind-furnace. The heat is slowly raised until the crucible becomes red-hot, after which it is urged to its maximum for an hour or more. When cold, the crucible is broken up, and the metallic button of manganese extracted.

Manganese is a grayish-white metal, resembling some varieties of cast-iron; it is hard and brittle, and destitute of magnetic properties. Its specific gravity is about 8. It is fusible with great difficulty, and, when free from iron, oxidizes in the air so readily, that it requires to be preserved in naphtha. Water is not sensibly decomposed by manganese in the cold. Dilute sulphuric acid dissolves it with great energy, evolving hydrogen.

The equivalent of manganese is assumed to be 27·67; its symbol is Mn.

Oxides of manganese.—Seven different oxides of this metal are described, but two out of the number are, probably, secondary compounds.

Protoxide	MnO
Sesquioxide	Mn_2O_3
Peroxide	MnO_2
Red Oxide	Mn_3O_4
Varvicite	Mn_4O_7
Manganic acid	MnO_3
Hypermanganic acid	Mn_2O_7

PROTOXIDE, MnO.—When carbonate of manganese is heated in a stream of hydrogen gas, or of vapor of water, the carbonic acid is disengaged, and a green colored powder left behind, which is the protoxide. Prepared at a dull red-heat only, the protoxide is so prone to absorb oxygen from the air, that it cannot be removed from the tube without change; but when made at a higher temperature, it is probably more stable. This oxide is a very powerful base, being isomorphous with magnesia and zinc; it dissolves quietly in

dilute acids, neutralizing them completely, and forming salts, which have often a beautiful pink color. When alkalies are added to solutions of these compounds, the white hydrated oxide first precipitated speedily becomes brown by passing to a higher state of oxidation.

SESQUIOXIDE. Mn_2O_3.—This compound occurs in nature in the state of hydrate; a very beautiful crystallized variety is found at Ilefeld, in the Hartz. It is produced artificially, by exposing to the air the hydrated protoxide, and forms the principal part of the residue left in the iron retort when oxygen gas is prepared by exposing the native peroxide to a moderate red heat. The color of the sesquioxide is brown or black, according to its origin or mode of preparation. It is a feeble base, isomorphous with alumina; for when gently heated with diluted sulphuric acid, it dissolves to a red liquid, which, on the addition of sulphate of potash or of ammonia, deposits octahedral crystals having the constitution of common alum; these are, however, decomposed by water. Strong nitric acid resolves this oxide into a mixture of protoxide and peroxide, the former dissolving, and the latter remaining unaltered, while hot oil of vitriol destroys it by forming protosulphate, and liberating oxygen gas. Heated with hydrochloric acid, chlorine is evolved, as with the peroxide, but to a smaller extent.

PEROXIDE, MnO_2.—The most common ore of manganese; it is found both massive and crystallized. It may be obtained artificially in the anhydrous state by gently calcining the nitrate, or in combination with water, by adding solution of bleaching powder to a salt of the protoxide. Peroxide of manganese has a black color, is insoluble in water, and refuses to unite with acids. It is decomposed by hot hydrochloric acid and by oil of vitriol, in the same manner as the sesquioxide.

As this substance is an article of commerce of considerable importance, being used in very large quantity for making chlorine, and as it is subject to great alteration of value from an admixture of the sesquioxide, it becomes desirable to possess means of assaying different samples that may be presented, with a view of testing their fitness for the purposes of the manufacturer. One of the best and most convenient methods is the following:—50 grains of the mineral, reduced to very fine powder, are put into the little vessel employed in the analysis of carbonates,* together with about half an ounce of cold water, and 100 grains of strong hydrochloric acid; 50 grains of crystallized oxalic acid are then added, the cork carrying the chloride of calcium tube is fitted, and the whole quickly weighed or counterpoised. The application of a gentle heat suffices to determine the action; the disengaged chlorine converts the oxalic acid into carbonic acid, with the help of the elements of water. Two equivalents of carbonic acid, representing one of chlorine, and consequently one of peroxide of manganese. Now the equivalent of the latter substance, 43·67, is so nearly equal to twice that of carbonic acid, 44, that the loss of weight suffered by the apparatus when the reaction has become complete, and the residual gas has been driven off by momentary ebullition, may be taken to represent the quantity of real peroxide in the 50 grains of the sample.

RED OXIDE, Mn_3O_4, or probably, $MnO + Mn_2O_3$.—This oxide is also found native, and is produced artificially by heating to whiteness the peroxide or sesquioxide, or by exposing the protoxide or carbonate to a red-heat in an open vessel. It is a reddish brown substance, incapable of forming salts, and acted upon by acids in the same manner as the two higher oxides already described. Borax and glass in a fused state dissolve this substance, and acquire the color of the amethyst.

* See page 201.

VARVICITE, Mn_4O_7, or $Mn_2O_3+2MnO_2$.—A natural production, discovered by Mr. Philips, among certain specimens of manganese-ore from Warwickshire; it has also been found at Ilefeld. It much resembles the peroxide, but is harder and more brilliant, and contains water. By a strong heat, varvicite is converted into red oxide, with disengagement of aqueous vapor and oxygen gas.

CHLORIDE OF MANGANESE, $MnCl$.—This salt may be prepared in a state of purity from the dark brown liquid residue of the preparation of chlorine from peroxide of manganese and hydrochloric acid, which often accumulates in the laboratory to a considerable extent in the course of investigation; from the pure chloride, the carbonate, and all the other salts, can be conveniently obtained. The liquid referred to consists chiefly of the mixed chlorides of manganese and iron; it is filtered, evaporated to perfect dryness, and then slowly heated to dull ignition in an earthen vessel, with constant stirring. The chloride of iron is thus either volatilized or converted by the remaining water into insoluble peroxide, while the manganese-salt is unaffected. On treating the grayish-looking powder thus obtained with water, the chloride of manganese is dissolved out, and may be separated by infiltration from the oxide of iron. Should a trace of the latter yet remain, it may be got rid of by boiling the liquid for a few minutes with a little carbonate of manganese. The solution of chloride has usually a delicate pink color, which becomes very manifest when the salt is evaporated to dryness. A strong solution deposits rose-colored tabular crystals, which contain 4 equivalents of water; these are very soluble and deliquescent. The chloride is fusible at a red heat, is decomposed slightly at that temperature by contact of air, and is dissolved by alcohol, with which it forms a crystallizable compound.

SESQUICHLORIDE, Mn_2Cl_3.—When precipitated sesquioxide of manganese is put into cold dilute hydrochloric acid, it dissolves quietly, forming a red solution of sesquichloride. Heat disengages chlorine, and occasions the production of protochloride.

SULPHATE OF PROTOXIDE OF MANGANESE, MnO, SO_3+7HO.—A beautiful rose-colored and very soluble salt, isomorphous with sulphate of magnesia. It is prepared on a large scale for the use of the dyer, by heating, in a close vessel, peroxide of manganese and coal, and dissolving the impure protoxide thus obtained in sulphuric acid, with the addition of a little hydrochloric acid towards the end of the process. The solution is evaporated to dryness, and again exposed to a red-heat, by which the persulphate of iron is decomposed. Water then dissolves out the pure sulphate of manganese, leaving the oxide of iron behind.* The salt is used to produce a permanent brown dye, the cloth steeped in the solution being afterwards passed through a solution of bleaching-powder, by which the protoxide is changed to insoluble hydrate of the peroxide. Sulphate of manganese sometimes crystallizes with five equivalents of water. It forms a double salt with sulphate of potash.

CARBONATE OF MANGANESE.—Prepared by precipitating the protochloride by an alkaline carbonate. It is insoluble and buff-colored, or sometimes nearly white. Exposed to heat, it loses carbonic acid, and absorbs oxygen.

MANGANIC ACID, MnO_3.—When an oxide of manganese is fused with an alkali, an additional quantity of oxygen is taken up from the air, and a deep green saline mass results, which contains a salt of the new acid, thus formed under the influence of the base. The addition of nitre, or chlorate of potash, facilitates the production of manganic acid. Water dissolves this compound very readily, and the solution, concentrated by evaporation in vacuo, yields green crystals.

* Graham, Elements, p. 372.

HYPERMANGANIC ACID.—Mn_2O_7.—When manganate of potash, free from any great excess of alkali, is put into a large quantity of water, it is resolved into hydrated peroxide of manganese, which subsides, and a deep purple liquid, containing hypermanganate of potash. This effect is accelerated by heat. The changes of color accompanying this decomposition are very remarkable, and have procured for the substance the name *mineral chameleon;* excess of alkali hinders, in some measure, the reaction, by conferring greater stability on the manganate. Hypermanganate of potash is easily prepared on a considerable scale. Equal parts of very finely powdered peroxide of manganese and chlorate of potash are mixed with rather more than one part of hydrate of potash dissolved in a little water, and the whole exposed, after evaporation to dryness, to a temperature just short of ignition. The mass is treated with hot water, the insoluble oxide separated by decantation, and the deep purple liquid concentrated by heat, until crystals form upon the surface; it is then left to cool. The crystals have a dark purple color, and are not very soluble in cold water. The manganates and hypermanganates are decomposed by contact with organic matter; the former are said to be isomorphous with the sulphates, and the latter with the hyperchlorates.

Salts of the protoxide of manganese are very easily distinguished by reagents.

The caustic alkalis, and ammonia, give white precipitates, insoluble in excess, quickly becoming brown.

The carbonates, and carbonate of ammonia, give white precipitates, but little subject to change.

Sulphuretted hydrogen gives no precipitate, but sulphuret of ammonium throws down insoluble, flesh-colored sulphuret of manganese, which is very characteristic.

Ferrocyanide of potassium gives a white precipitate.

Manganese is also easily detected by the blow-pipe; it gives with borax an amethystine bead in the outer or oxidizing flame, and a colorless one in the inner flame.

IRON.

This is by very far the most important member of the group of metals under discussion; there are few substances which yield to it in interest, when it is considered how very intimately the knowledge of the properties and uses of iron is connected with human civilization.

Metallic iron is of exceedingly rare occurrence; it has been found at Canaan, in Connecticut,* forming a vein about two inches thick in mica-slate, and it very frequently enters into the composition of those extraordinary stones known to fall from the air, called *meteorites*. Isolated masses of soft malleable iron also, of large dimensions, lie loose upon the surface of the earth in South America and elsewhere, and are presumed to have had a similar origin; these latter contain, in common with the iron of the undoubted meteorites, nickel. In an oxidized condition, the presence of iron may be said to be universal; it constitutes great part of the common coloring matter of rocks and soils; it is contained in plants, and forms an essential component of the blood of the animal body. In the state of bisulphate it is also very common. Pure iron may be prepared, according to Mitscherlich, by introducing into a Hessian crucible 4 parts of fine iron wire cut small, and 1 part of black oxide of iron. This is covered with a mixture of white sand, lime,

* Phillip's Mineralogy, 4th edit. p. 208.

and carbonate of potash, in the proportions used for glass-making, and a cover being closely applied, the crucible is exposed to a very high degree of heat. A button of pure metal is thus obtained, the traces of carbon and silicon present in the wire having been removed by the oxygen of the oxide.

Pure iron has a white color and perfect lustre; it is extremely soft and tough, and has a specific gravity of 7·8. The crystalline form is probably the cube, to judge from appearances now and then exhibited. In good bar-iron or wire a distinct fibrous texture may always be observed when the metal has been attacked by rusting, or by the application of an acid, and upon the perfection of this fibre much of its strength and value depends. Iron is the most tenacious of all the metals, a wire $\frac{1}{38}$ of an inch in diameter bearing a weight of 60 lbs. It is very difficult of fusion, and before becoming liquid passes through a soft or pasty condition. Pieces of iron pressed or hammered together in this state, cohere into a single mass; the operation is termed *welding*, and is usually performed by sprinkling a little sand over the heated metal, which combines with the superficial film of oxide, forming a fusible silicate, which is subsequently forced out from between the pieces of iron by the pressure applied; clean surfaces of metal are thus presented to each other, and union takes place without difficulty.

Iron does not oxidize in dry air at common temperatures; heated to redness, it becomes covered with a scaly coating of black oxide, and at a high white heat, burns brilliantly, producing the same substance; in oxygen gas the combustion occurs with still greater ease. The finely-divided spongy metal, prepared by reducing the red oxide by hydrogen gas, takes fire spontaneously in the air.* Pure water, free from air and carbonic acid, does not tarnish a surface of polished iron, but the combined agency of free oxygen and moisture speedily leads to the production of rust, which is a hydrate of the peroxide. The rusting of iron is wonderfully promoted by the presence of a little acid vapor. At a red heat iron decomposes water, evolving hydrogen, and passing into the black oxide. Dilute sulphuric and hydrochloric acids dissolve it freely with separation of hydrogen. Iron is strongly magnetic up to a red-heat, when it loses all traces of that remarkable property.

The equivalent of iron is 27·14, and its symbol Fe.

Four compounds of iron and oxygen are described.

Protoxide . .	FeO
Sesquioxide (peroxide)	Fe_2O_3
Black oxide . .	Fe_3O_4
Ferric acid . .	FeO_3

PROTOXIDE. FeO.—This is a very powerful base, neutralizing acids completely, and isomorphous with magnesia, oxide of zinc, &c. It is almost unknown in a separate state, from its extreme proneness to absorb oxygen and pass into the sesquioxide. When a salt of this substance is mixed with caustic alkali or ammonia, a bulky whitish precipitate of hydrate of the protoxide falls, which becomes nearly black when boiled, possibly from the separation of water. This hydrate exposed to the air, very rapidly changes, becoming green and ultimately red-brown. The soluble salts of protoxide of iron have commonly a delicate pale green color, and a nauseous *metallic* taste.

PEROXIDE. Fe_2O_3.—A feeble base, isomorphous with alumina. Peroxide of iron occurs native, most beautifully crystallized as specular iron ore in the Island of Elba, and elsewhere; also as red and brown *hæmatites*, the latter being a hydrate. It is artificially prepared by precipitating a solution of persulphate or perchloride or iron by excess of ammonia, and washing, drying,

* When obtained at a heat below redness.—R. B.

and igniting the yellowish brown hydrate thus produced; fixed alkali must not be used in this operation, as a portion is retained by the oxide. In fine powder, this oxide has a full red color, and is used as a pigment, being prepared for the purpose by calcination of the protosulphate; the tint varies somewhat with the temperature to which it has been exposed. This oxide is unaltered in the fire, although easily reduced at a high temperature by carbon or hydrogen. It dissolves in acids, with difficulty after strong ignition, forming a series of reddish salts, which have an acid reaction and an astringent taste. Peroxide of iron is not acted upon by the magnet.*

Black oxide; magnetic oxide; loadstone. Fe_3O_4, or probably $FeO+Fe_2O_3$.—A natural product, one of the most valuable of the iron ores, often found in regular octahedral crystals, which are magnetic. It may be prepared by mixing due proportions of a proto and a per-salt of iron, precipitating them by excess of alkali and then boiling the mixed hydrates, when the latter unite to a black sandy substance, consisting of minute crystals of the magnetic oxide. This oxide is the chief product of the oxidation of iron at a high temperature in the air and in aqueous vapor. It is incapable of forming salts.

Ferric acid. FeO_3.—A very remarkable compound of recent discovery. The simplest mode of preparing it is to heat to full redness, for an hour, in a covered crucible, a mixture of one part of pure peroxide of iron, and four parts of dry nitre. The brown, porous, deliquescent mass is treated when cold with ice-cold water, by which a deep amethystine red solution of ferrate of potash is obtained. This gradually decomposes even in the cold, evolving oxygen gas, and depositing sesquioxide; by heat the decomposition is very rapid. The solution of ferrate of potash gives no precipitate with salts of lime, magnesia, or strontia, but when mixed with one of baryta, a deep crimson, insoluble compound falls, which is a ferrate of that base, and is very permanent.

Protochloride of iron. $FeCl$.—Formed by transmitting dry hydrochloric acid gas over red-hot metallic iron, or by dissolving iron in hydrochloric acid. The latter solution yields, when duly concentrated, green crystals of the protochloride, containing 4 equivalents of water; they are very soluble and deliquescent, and rapidly poroxidize in the air.

Sesquichloride of iron. Fe_2Cl_3.—Usually prepared by dissolving peroxide in hydrochloric acid. The solution, evaporated to a syrupy consistence, deposits red, hydrated crystals, which are very soluble in water, and alcohol. It forms double salts with chloride of potassium and sal ammoniac. When evaporated to dryness and strongly heated, much of the chloride is decomposed, yielding peroxide and hydrochloric acid; the remainder sublimes, and afterwards condenses in the form of small brilliant red crystals, which deliquesce rapidly. The solution of sesquichloride of iron is capable of dissolving a large excess of recently precipitated hydrate of the peroxide, by which it acquires a much darker color. Anhydrous sesquichloride of iron is also produced by the action of chlorine upon the heated metal.

Protiodide of iron. FeI.—This is an important medicinal preparation; it is easily made by digesting iodine with water and metallic iron. The solution is pale green, and yields, on evaporation, crystals resembling those of the chloride, which rapidly peroxidize on exposure to air. It is best preserved in solution in contact with excess of iron.† A periodide of iron exists, which is yellowish red, and soluble.

* In the form of hydrate, Fe_2O_3+3HO, as recently precipitated from the persulphate by ammonia, it constitutes the antidote for arsenious acid. The affinity for water in this case is not strong—the hydrate gradually decomposing even when kept under water, its color passing from yellowish brown to red.—R. B.

† Or protected from the action of oxygen by pure honey, or other saccharine substance, in the proportion of one part to three of the solution.—R. B.

SULPHURETS OF IRON.—Several compounds of iron and sulphur are described; of these the two most important are the following. *Protosulphuret*, FeS, is a blackish, brittle substance, attracted by the magnet, formed by heating together iron and sulphur. It is dissolved by dilute acids with evolution of sulphuretted hydrogen gas, and is constantly employed for that purpose in the laboratory, being made by projecting into a red-hot crucible a mixture of 2½ parts of sulphur and 4 parts of iron filings or borings of cast-iron, and excluding the air as much as possible. The same substance is formed when a bar of white-hot iron is brought in contact with sulphur. The *bisulphuret of iron*, FeS_2, is a natural product, occurring in rocks of all ages, and evidently formed in many cases by the gradual deoxidation of sulphate of iron by organic matter. It has a brass-yellow color, is very hard, not attracted by the magnet, and not acted upon by dilute acids. Exposed to heat, sulphur is expelled, and an intermediate sulphuret, the analogue probably of the black oxide, produced. This substance also occurs native, under the name of *magnetic pyrites*. The bisulphuret is now much used in the manufacture of sulphuric acid.

Compounds of iron with phosphorus, carbon, and silicon exist, but little is known respecting them in a definite state. The carburet is contained in cast-iron and in steel, to which it communicates ready fusibility; the silicate is also found in cast-iron. Phosphorus is a very hurtful substance in bar-iron, as it renders it brittle or *cold-short*.

PROTOSULPHATE OF IRON; GREEN VITRIOL. FeO, SO_3+7HO.—This beautiful and important salt may be obtained by directly dissolving iron in dilute sulphuric acid; it is generally prepared, however, and that on a very large scale, by contact of air and moisture with common iron pyrites, which, by absorption of oxygen, readily furnishes the substance in question. Heaps of this material are exposed to the air until the decomposition is sufficiently advanced; the salt produced is then dissolved out by water, and the solution made to crystallize. It forms large green crystals, of the composition above stated, which slowly effloresce and peroxidize in the air; it is soluble in about twice its weight of cold water. Crystals containing 4, and also 2 equivalents of water, have been obtained. Protosulphate of iron forms double salts with the sulphates of potash and ammonia.

PERSULPHATE OF IRON. $Fe_2O_3, 3SO_3$.—Prepared by adding to a solution of the proto-salt exactly one-half as much sulphuric acid as it already contains, raising the liquid to the boiling point, and then dropping in nitric acid until the solution ceases to blacken by such addition. The red liquid thus obtained furnishes, on evaporation to dryness, a buff-colored, amorphous mass, which, when put into water, very slowly dissolves. With the sulphates of potash and ammonia, this salt yields compounds having the form and constitution of the alums; the crystals are nearly destitute of color. These latter are decomposed by water, and sometimes by long keeping when in a dry state. They are best prepared by exposing to spontaneous evaporation a solution of persulphate of iron to which sulphate of potash or of ammonia has been added.

PROTONITRATE OF IRON.—FeO, NO_5.—When dilute cold nitric acid is made to act to saturation upon protosulphuret of iron, and the solution evaporated in vacuo, pale green and very soluble crystals of protonitrate are obtained, which are very subject to alteration. *Pernitrate* is readily formed by pouring nitric acid, slightly diluted, upon iron; it is a deep red liquid, apt to deposit insoluble sub-salt, and is used in dyeing.

PROTOCARBONATE OF IRON. FeO, CO_2.—The white precipitate obtained by mixing solutions of proto-salt of iron and alkaline carbonate; it cannot be washed and dried without losing carbonic acid and absorbing oxygen. This substance occurs in nature as *spathose iron ore*, associated with variable

quantities of carbonate of lime and of magnesia; and also in the common *clay iron-stone*, from which nearly all the British iron is made. It is often found in mineral waters, being soluble in excess of carbonic acid; such waters are known by the rusty matter they deposit. No carbonate of the peroxide is known.

The phosphates of iron are all insoluble.

Salts of the protoxide of iron are thus distinguished:—

Caustic alkalis, and ammonia, give nearly white precipitates, insoluble in excess of the reagent, rapidly becoming green, and ultimately brown, by exposure to air.

Alkaline carbonates, and carbonate of ammonia, throw down the white carbonate, also very subject to change.

Sulphuretted hydrogen gives no precipitate, but sulphuret of ammonium throws down black protosulphuret of iron, soluble in dilute acids.

Ferrocyanide of potassium gives a nearly white precipitate, becoming deep blue on exposure to air.

Salts of the peroxide are thus characterized:—

Caustic alkalis, and ammonia, give foxy-red precipitates of hydrated peroxide, insoluble in excess.

The carbonates behave in a similar manner, the carbonic acid escaping.

Sulphuretted hydrogen gives a nearly white precipitate of sulphur, and reduces the peroxide to protoxide.

Sulphuret of ammonium gives a black precipitate, slightly soluble in excess.

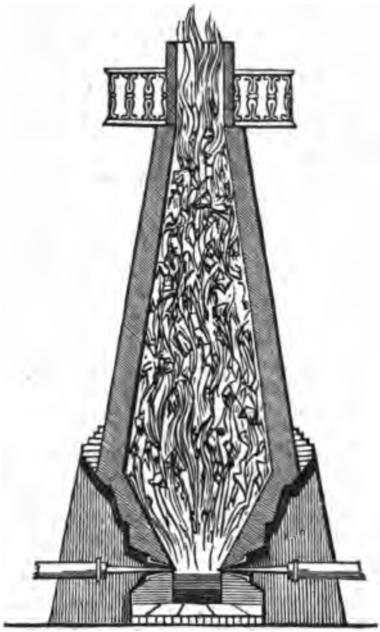
Ferrocyanide of potassium yields Prussian blue.

Iron manufacture.—This most important branch of industry consists, as now conducted, of two distinct parts, viz., the production from the ore of a fusible carburet of iron, and the subsequent decomposition of the carburet, and its conversion into pure or malleable iron.

The clay iron ore is found in association with coal, forming thin beds or nodules; it consists, as already mentioned, of carbonate of iron mixed with clay; sometimes lime and magnesia are also present. It is broken in pieces, and exposed to heat in a furnace resembling a lime-kiln, by which the water and carbonic acid are expelled, and the ore rendered dark-colored, denser, and also magnetic; it is then ready for reduction. The furnace in which this operation is performed is usually of very large dimensions, fifty feet or more in height, and constructed of brickwork with great solidity, the interior being lined with excellent fire-bricks; the figure will be at once understood from the sectional drawing. (Fig. 140.) The furnace is close at the bottom, the fire being maintained by a powerful artificial blast introduced by two or three *tuyere-pipes*, as shown in the section. The materials consisting of due proportions of coke or carbonized coal, roasted ore, and limestone, are constantly supplied from the top, the operation proceeding continuously night and day, often for years, or until the furnace is judged to require repair. In the upper part of the furnace, where the temperature is still very high, and where combustible gases abound, the iron of the ore is probably reduced to the metallic state, being disseminated through the earthy matter of the ore; as the whole sinks down and attains a still higher degree of heat, the iron becomes converted into carburet by *cementation*, while the silica and alumina unite with the lime, purposely added, to a kind of glass or *slag*, nearly free from oxide of

iron. The carburet and slag, both in a melted state, reach at last the bottom of the furnace, where they arrange themselves in the order of their densities; the slag flows out at certain apertures contrived for the purpose, and the iron is discharged from time to time, and suffered to run into rude moulds of sand, by opening an orifice at the bottom of the recipient, previously stopped with clay. Such is the origin of crude or cast-iron, of which there are several varieties, distinguished by differences of color, hardness, and composition, and known by the names of *gray*, *black*, and *white* iron. The first is for most purposes the best, as it admits of being filed and cut with perfect ease. The black and gray kinds probably contain a mechanical admixture of graphite, which separates during solidification.

Fig. 140.



A great improvement has been recently made in the above-described process, by substituting raw coal for coke, and blowing hot air, instead of cold, into the furnace. This is effected by causing the air, on leaving the blowing-machine, to circulate through a system of red-hot iron pipes, until its temperature becomes high enough to melt lead. This alteration has already effected a prodigious saving in fuel, without, it appears, any injury to the quality of the product.

The conversion of cast into bar-iron is effected by an operation called *puddling;* previous to which, however, it commonly undergoes a process, the theory of which is not very intelligible. It is re-melted, and suddenly cooled, by which it becomes white, crystalline, and exceedingly hard; in this state it

is called *fine-metal*. The puddling process is conducted in an ordinary reverberatory furnace, into which the charge of fine metal is introduced by a side aperture. This is speedily melted by the flame, and its surface covered with a coat of oxide. The workman then, by the aid of an iron tool, diligently stirs the melted mass, so as intimately to mix the oxide with the metal; he now and then also throws in a little water, with the view of promoting more rapid oxidation. Small jets of blue flame soon appear upon the surface of the iron, and the latter, after a time, begins to lose its fluidity, and acquires, in succession, a pasty and a granular condition. At this point, the fire is strongly urged, the sandy particles once more cohere, and the contents of the furnace now admit of being formed into several large balls or masses, which are then withdrawn, and placed under an immense hammer, moved by machinery, by which each becomes quickly fashioned into a rude bar. This is re-heated, and passed between grooved cast-iron rollers, and drawn out into a long bar or rod. To make the best iron, the bar is cut into a number of pieces, which are afterwards bound together, again raised to a welding heat, and hammered or rolled into a single bar; and this process of *piling* or *fagotting* is sometimes twice or thrice repeated, the iron becoming greatly improved thereby.

The general nature of the change in the puddling furnace is not difficult to explain. Cast-iron consists essentially of iron in combination with carbon and silicon; when strongly heated with oxide of iron, those compounds undergo decomposition, the carbon and silicon becoming oxidized at the expense of the oxygen of the oxide. As this change takes place, the metal gradually loses its fusibility, but retains a certain degree of adhesiveness, so that when at last it comes under the tilt-hammer, or between the rollers, the particles of iron become agglutinated into a solid mass, while the ready-fusible silicate of the oxide is squeezed out and separated.

All these processes are, in Great Britain, performed with coal or coke, but the iron obtained is, in many respects, inferior to that made in Sweden and Russia from the magnetic oxide, by the use of wood charcoal;—a fuel too dear to be extensively employed in England. Plate iron is, however, sometimes made with charcoal.

Steel.—A very remarkable, and most useful substance, prepared by heating iron in contact with charcoal. Bars of Swedish iron are imbedded in charcoal powder, contained in a large rectangular crucible or chest of some substance, capable of resisting the fire, and exposed for many hours to a full red heat. The iron takes up, under these circumstances, from 1·3 to 1·7 per cent. of carbon, becoming harder, and at the same time fusible, with a certain diminution, however, of malleability. The active agent in this cementation process is probably carbonic oxide; the oxygen of the air in the crucible combines, with the carbon, to form that substance, which is afterwards decomposed by the heated iron, one half of its carbon being abstracted by the latter. The carbonic acid thus formed takes up an additional dose of carbon from the charcoal, and again becomes carbonic oxide, the oxygen, or rather the carbonic acid, acting as a carrier between the charcoal and the metal. The product of this operation is called *blistered* steel, from the blistered and rough appearance of the bars; the texture is afterwards improved and equalized by welding a number of these bars together, and drawing the whole out under a light tilt-hammer.

The most perfect kind of steel is that which has undergone fusion, having been cast into ingot-moulds, and afterwards hammered; of this all fine cutting instruments are made; it is difficult to force, requiring great skill and care on the part of the operator.

Steel may also be made directly from some particular varieties of cast-iron, as that from spathose iron ore, containing a little manganese. The metal is

retained, in a melted state, in the hearth of a furnace while a stream of air plays upon it, and causes partial oxidation; the oxide produced reacts, as before stated, on the carbon of the iron, and withdraws a portion of that element. When a proper degree of stiffness or pastiness is observed in the residual metal, it is withdrawn, and hammered or rolled into bars. The *wootz*, or native steel of India, is probably made in this manner. Annealed cast-iron, sometimes called *run-steel*, is now much employed as a substitute for the more costly products of the forge; the articles, when cast, are imbedded in powdered iron-ore, or some earthy material, and, after being exposed to a moderate red heat for some time, are allowed slowly to cool, by which a very extraordinary degree of softness and malleability is attained. It is very possible that some little decarbonization may take place during this process.

The most remarkable property of steel is that of becoming exceedingly hard when quickly cooled; when heated to redness, and suddenly quenched in cold water, steel, in fact, becomes capable of scratching glass with facility; if re-heated to redness, and once more left to cool slowly, it again becomes nearly as soft as ordinary iron, and, between these two conditions, any required degree of hardness may be attained. The articles, forged into shape, are first hardened in the manner described; they are then *tempered*, or *let down*, by exposure to a proper degree of annealing heat, which is often judged of by the color of the thin film of oxide which appears on the polished surface. Thus, a temperature of about 430° F., indicated by a faint straw-color, gives the proper temper for razors; that for scissors, pen-knives, &c., will be comprised between 470° and 490°, and be attained by a full yellow or brown tint. Swords and watch-springs require to be softer and more elastic, and must be heated to 550° or 560°, or until the surface becomes deep blue. Attention to these colors has now become of less importance, as metal baths are often substituted for the open fire in this operation.

NICKEL.

Nickel is found in tolerable abundance in some of the metal-bearing veins of the Hartz mountains, and in a few other localities, chiefly as arseniuret, the *kupfernickel* of mineralogists, so called from its yellowish-red color; the word *nickel* is a term of detraction, having been applied by the old German miners to what was looked upon as a kind of false copper ore.

The artificial, or perhaps rather, fused product, called *speiss*, is nearly the same substance, and may be employed as a source of the nickel-salts. This metal is found in meteoric iron, as already mentioned.

Nickel is easily prepared by exposing the oxalate to a high white heat, in a crucible lined with charcoal. It is a white, malleable metal, having a density of 8·8, a high melting-point, and a less degree of oxidability than iron, since it is but little attacked by dilute acids. Nickel is strongly magnetic, but loses this property when heated to 660°. This metal forms two oxides, only one of which is basic. The equivalent of nickel is 29·57; its symbol is Ni.

Protoxide of nickel, NiO.—This compound is prepared by heating to redness the nitrate, or by precipitating a soluble salt with caustic potash, and washing, drying, and igniting the apple-green hydrated oxide thrown down. It is an ash-gray powder, freely soluble in acids, which it completely neutralizes, being isomorphous with magnesia, and the other members of the same group. The salts of this substance have usually a beautiful green color.

Peroxide, or superoxide of nickel, Ni_2O_3.—The peroxide is a black insoluble substance, prepared by passing chlorine through the hydrated oxide suspended in water; chloride of nickel is formed, and the oxygen of the oxide decomposed transferred to a second portion. It is also produced when

a salt of nickel is mixed with a solution of bleaching powder. The peroxide is decomposed by heat, and evolves chlorine when put into hot hydrochloric acid.

CHLORIDE OF NICKEL, NiCl.—This is easily prepared by dissolving oxide of nickel in hydrochloric acid. A green solution is obtained which furnishes crystals of the same color, containing water. When rendered anhydrous by heat, the chloride is yellow, unless it contain cobalt, in which case it has a tint of green.

SULPHATE OF NICKEL, NiO, SO_3+7HO.—This is the salt from which the other compounds of nickel are commonly prepared; the following is said to be a good process for obtaining it from the crude arseniuret. The speiss, which should be free from cobalt, is reduced to very fine powder, and roasted, at a dull red-heat, in an open vessel, a little charcoal-powder being added from time to time. The residue, which principally consists of arseniate of the oxide, is mixed with carbonate of soda and a little nitre, and the whole heated to fusion in an earthen crucible. Any undecomposed arseniuret is thus oxidized, while the arsenic acid is transferred to the alkali. The arseniate and superfluous carbonate of soda are then separated from the oxide of nickel by solution in water, and the latter is dissolved in dilute sulphuric acid. This solution is boiled with chalk (carbonate of lime), which does not act upon the sulphate of nickel, but precipitates oxide of iron and other substances completely. Lastly, the purification is completed by a stream of sulphuretted hydrogen, which separates any copper, &c., which may happen to be present.

The sulphate is deposited from a moderately strong solution in green prismatic crystals, containing 7 equivalents of water, which require about 3 parts of cold water for solution. Crystals with 6 equivalents of water have also been obtained. It forms, with the sulphate of potash and ammonia, beautiful double salts, NiO,SO_3+KO,SO_3+6HO and NiO,SO_3+NH_4O, SO_3+6HO. When a strong solution of oxalic acid is mixed with sulphate of nickel, a pale bluish-green precipitate of oxalate falls; after some time, very little nickel remaining in solution. The oxalate can thus be obtained for preparing the metal.

CARBONATE OF NICKEL.—When solutions of sulphate of nickel and of carbonate of soda are mixed, a pale green precipitate falls, which is a combination of carbonate and hydrate of nickel. It is readily decomposed by heat.

The salts of nickel are well characterized by their behavior with reagents.

Caustic alkalis give a pale apple-green precipitate of hydrate, insoluble in excess.

Ammonia affords a similar precipitate, which is soluble in excess, with deep purplish-blue color.

Carbonate of potash and soda give pale green precipitates.

Carbonate of ammonia, a similar precipitate, soluble in excess, with blue color.

Ferrocyanide of potassium gives a greenish-white precipitate.

Sulphuretted hydrogen occasions no change.

Sulphuret of ammonium throws down a black sulphuret of nickel.

The chief use of nickel in the arts is in the preparation of a white alloy, sometimes called German silver, made by melting together 100 parts of copper, 60 of zinc, and 40 of nickel. This alloy is very malleable, and takes a high polish.

COBALT.

This substance bears, in many respects, an extraordinary resemblance to the metal last described; it is constantly associated with it in nature, and may be obtained from its compounds by similar means. Cobalt is a white brittle metal, having a specific gravity of 8·5, and a very high melting-point. It is unchanged in the air, and but feebly attacked by dilute hydrochloric and sulphuric acids. When quite pure, cobalt is not magnetic. There are two oxides of this metal, corresponding in properties and constitution with those of nickel.

The equivalent of cobalt is 29·52; its symbol is Co.

Protoxide of cobalt.—CoO.—This is gray powder, very soluble in acids, and is a strong base, isomorphous with magnesia, affording salts of a fine red tint. It is prepared by precipitating sulphate of cobalt with carbonate of soda, and washing and drying and igniting the precipitate. When the cobalt-solution is mixed with caustic potash, a beautiful blue precipitate falls, which when heated, becomes violet, and at length dirty red, from a change in the state of hydration.

Peroxide of cobalt.—Co_2O_3.—The peroxide is a black, insoluble, neutral powder, obtained by mixing solutions of cobalt and of chloride of lime.

Chloride of cobalt.—$CoCl$.—The chloride is easily prepared by dissolving the oxide in hydrochloric acid; it gives a deep rose-red solution, which, when sufficiently strong, deposits hydrated crystals of the same color. When the liquid is evaporated by heat to a very small bulk, it deposits anhydrous crystals which are blue; these latter by contact with water again dissolve to a red liquid. A dilute solution of chloride of cobalt constitutes the well-known *blue sympathetic ink;* characters written on paper with this liquid are invisible from their paleness of color until the salt has been rendered anhydrous by exposure to heat, when the letters appear blue. When laid aside, moisture is absorbed, and the writing once more disappears. Green sympathetic ink is a mixture of the chlorides of cobalt and nickel.

Sulphate of cobalt.—CoO,SO_3+7HO.—This salt may be directly prepared from *cobalt-glance*, the native arseniuret, which should be chosen free from nickel, as much difficulty occurs in separating these two metals. The ore is pulverized and roasted wilh a little charcoal powder; the impure oxide is dissolved in sulphuric acid, to which a little hydrochloric acid is added; the solution is boiled with chalk, treated with sulphuretted hydrogen, and evaporated to the crystallizing point. The crystals are red; they require for solution 24 parts of cold water, and are identical in form with those of sulphate of magnesia. The sulphate of cobalt forms double salts with the sulphates of potash and ammonia, which contain as usual six equivalents of water.

A solution of oxalic acid added to one of sulphate of cobalt occasions, after some time, the separation of nearly the whole of the base in the state of oxalate.

Carbonate of cobalt.—The alkaline carbonates produce in solutions of cobalt a pale peach blossom colored precipitate of combined carbonate and hydrate, containing $3CoO,HO+2CoCO_2+HO$.

The salts of cobalt have the following characters:—

Solution of potash gives a blue precipitate, changing by heat to violet and red.

Ammonia gives a blue precipitate, soluble with difficulty in excess with brownish red color.

Carbonate of soda affords a pink precipitate.

Carbonate of ammonia, a similar compound, soluble in excess.
Ferrocyanide of potassium gives a grayish-green precipitate.
Sulphuretted hydrogen produces no change.
Sulphuret of ammonium throws down black sulphuret of cobalt.

Oxide of cobalt is remarkable for the magnificent blue color it communicates to glass; indeed this is a character by which its presence may be most easily detected, a very small portion of the substance to be examined being fused with borax on a loop of platinum wire before the blow-pipe. The substance called *smalt*, used as a pigment, consists of glass colored by oxide of cobalt; it is thus made:—the cobalt ore is roasted until nearly free from arsenic, and then fused with a mixture of carbonate of potash and quartz-sand free from oxide of iron. Any nickel that may happen to be contained in the ore then subsides to the bottom of the crucible as arseniuret; this is the *speiss*, of which mention has already been made. The glass, when complete, is removed and poured into cold water; it is afterwards ground to powder and elutriated. *Cobalt-ultramarine* is a fine blue color prepared by mixing 16 parts of freshly-precipitated alumina with 2 parts of phosphate or arseniate of cobalt: this mixture is dried and slowly heated to redness. By day-light the color is pure blue, but by artificial light it is violet. *Zaffer* is the roasted cobalt ore mixed with a quantity of siliceous sand, and reduced to fine powder; it is used in enamel painting. A mixture in due proportions of the oxides of cobalt, manganese and iron is used for giving a fine black color to glass.

ZINC.

Zinc is a somewhat abundant metal; it is found in the state of carbonate and sulphuret, associated with lead ores in many districts, both in Britain and on the continent; large supplies are obtained from Silesia. The native carbonate, or *calamine*, is the most valuable of the zinc ores, and is preferred for the extraction of the metal; it is first roasted to expel water and carbonic acid, mixed with fragments of coke or charcoal, and then distilled at a full red-heat in a large earthen retort; carbonic oxide escapes, while the reduced metal volatilizes, and is condensed by suitable means.

Zinc is a bluish-white metal, which slowly tarnishes in the air; it has a lamellar, crystalline structure, a density varying from 6·8 to 7·2, and is, under ordinary circumstances, brittle. Between 250° and 300° it is, on the contrary, malleable, and may be rolled or hammered without danger of fracture, and what is very remarkable, after such treatment, retains its malleability when cold;—the sheet-zinc of commerce is thus made. At 400° it is so brittle that it may be reduced to powder. At 773° it melts; at a bright red-heat it boils and volatilizes, and if air be admitted, burns with a splendid green light, generating the oxide. Dilute acids dissolve zinc very readily; it is constantly employed in this manner in preparing hydrogen gas.

The equivalent of zinc has been fixed at 33·; its symbol Zn.

Oxide of zinc.—ZnO.—Only one oxide of this metal is known to exist; it is a strong base, isomorphous with magnesia; it is prepared either by burning zinc in atmospheric air, or by heating to redness the carbonate. Oxide of zinc is a white, tasteless powder, insoluble in water, but freely dissolved by acids. When heated it is yellow.

Sulphate of zinc; white vitriol.—ZnO,SO_3+7HO.—This salt is hardly to be distinguished by the eye from sulphate of magnesia; it is prepared either by dissolving the metal in dilute sulphuric acid, or more economically

by roasting the native sulphuret, or *blende*, which, by absorption of oxygen, becomes in great part converted into sulphate of the oxide. The altered mineral is thrown hot into water, and the salt obtained by evaporating the clear solution. Sulphate of zinc has an astringent, metallic taste, and is used in medicine as an emetic. The crystals dissolve in 2½ parts of cold, and in a much smaller quantity of hot water. Crystals containing 6 equivalents of water have been observed. Sulphate of zinc forms double salts with the sulphates of potash and ammonia.

CARBONATE OF ZINC.—ZnO,CO_2.—The neutral carbonate is found native; the white precipitate, obtained by mixing solutions of zinc and of alkaline carbonates, is a combination of carbonate and hydrate. When heated to redness it yields pure oxide of zinc.

CHLORIDE OF ZINC.—$ZnCl$.—The chloride may be prepared by heating metallic zinc in chlorine; by distilling a mixture of zinc-filings and corrosive sublimate: or, more easily, by dissolving zinc in hydrochloric acid. It is a nearly white, translucent, fusible substance, very soluble in water and alcohol, and very deliquescent. A strong solution of chloride of zinc is used as a bath for obtaining a graduated heat above 212°. Chloride of zinc unites with sal-ammoniac and chloride of potassium to double salts; the former of these, made by dissolving an equivalent of zinc in the requisite quantity of hydrochloric acid, and then adding an equivalent of sal-ammoniac, is very useful in tinning and soft-soldering copper and iron.

A salt of zinc is easily distinguished by appropriate reagents.

Caustic potash and soda give a white precipitate of hydrate, freely soluble in excess of alkali.

Ammonia behaves in the same manner; an excess re-dissolves the precipitate instantly.

The carbonates of potash and soda give white precipitates, insoluble in excess.

Carbonate of ammonia gives also a white precipitate, which is re-dissolved by an excess.

Ferrocyanide of potassium gives a white precipitate.

Sulphuretted hydrogen causes no change.

Sulphuret of ammonium throws down white sulphuret of zinc.

The applications of metallic zinc to the purposes of roofing, the construction of water-channels, &c., are well known; it is sufficiently durable, but inferior, in this respect, to copper.

CADMIUM.

This metal was discovered in 1817 by Stromeyer; it accompanies the ores of zinc, and, being more volatile than that substance, rises first in vapor when the calamine is subjected to distillation with charcoal. Cadmium resembles tin in color, but is somewhat harder; it is very malleable, has a density of 8·7, melts below 500°, and is nearly as volatile as mercury. It tarnishes but little in the air, but, when strongly heated, burns. Dilute sulphuric and hydrochloric acids act but little on this metal in the cold; nitric acid is its best solvent.

The equivalent of cadmium is 55·74; its symbol is Cd.

OXIDE OF CADMIUM, CdO.—The oxide may be prepared by igniting either the carbonate or the nitrate; in the former case it has a pale brown color, and

in the latter a much darker tint, and a crystalline aspect. Oxide of cadmium is infusible; it dissolves in acids, producing a series of colorless salts.

Sulphate of cadmium, CdO, SO_3+4HO.—This is easily obtained by dissolving the oxide or carbonate in dilute sulphuric acid; it is very soluble in water, and forms double salts with the sulphates of potash and of ammonia, which contain CdO, SO_3+KO, SO_3+6HO, and the latter $CdO, SO_3+NH_4O, SO_3+6HO$.

Chloride of cadmium, $CdCl$.—This is a very soluble salt, crystallizing in small four-sided prisms.

Sulphuret of cadmium is a very characteristic compound, of a bright yellow color, fusible at a high temperature. It is obtained by passing sulphuretted hydrogen gas through a solution of the sulphate, nitrate, or chloride.

The salts of cadmium are thus distinguished:—

Caustic alkalis give a white precipitate of hydrated oxide, insoluble in excess.

Ammonia gives a similar white precipitate, readily soluble in excess.

The alkaline carbonates, and carbonate of ammonium, throw down white carbonate of cadmium, insoluble in excess of either precipitant.

Sulphuretted hydrogen and sulphuret of ammonium precipitate the yellow sulphuret of cadmium.

BISMUTH.

Bismuth is found, chiefly in the metallic state, disseminated through an earthy matrix; from which it is separated by simple exposure to heat. The metal is highly crystalline, and very brittle; it has a reddish-white color, and a density of 9·9. Cubic crystals, of great beauty, may be obtained by slowly cooling a considerable mass of this substance until solidification has commenced, and then piercing the crust, and pouring out the fluid residue. Bismuth melts at about 500°, and volatilizes at a high temperature; it is little oxidized by the air, but burns when strongly heated with a bluish flame. Nitric acid, somewhat diluted, dissolves it freely.

The equivalent of bismuth is 70·96; its symbol is Bi.

Oxide of bismuth, BiO.—This is the base of all the salts. It is a straw-yellow powder, obtained by gently igniting the subnitrate. It is fusible at a high temperature, and in that state acts towards siliceous matter as a powerful flux.

Peroxide or superoxide of bismuth, Bi_2O_3.—The peroxide is a brown powder, obtained by boiling the above-described oxide with solution of hypochlorite of potash. (Bleaching liquid.) It is decomposed by heat, and does not unite with acids.

Nitrate of bismuth, BiO, NO_5+3HO.—When bismuth is dissolved in moderately strong nitric acid to saturation, and the whole left to cool, large, colorless, transparent crystals of the neutral nitrate are deposited. Water decomposes these crystals; an acid solution containing a little bismuth is obtained, and a brilliant white crystalline powder is left, which is a subnitrate containing BiO, NO_5+3BiO, HO. A solution of nitrate of bismuth, free from any great excess of acid, poured into a large quantity of cold water, yields an insoluble subnitrate, very similar in appearance to the above, but containing rather a smaller proportion of oxide of bismuth. This remarkable decomposition illustrates at once the basic property of water, and the feeble affinity of oxide of bismuth for acids, the nitric acid dividing itself between the two bases. The decomposition of a neutral salt by water is by no means an uncommon occurrence in the history of the metals; a solution of chloride of antimony exhibits

the same phenomenon, certain salts of mercury are affected in a similar manner, and other cases might perhaps be cited, less conspicuous, where the same change takes place to a smaller extent.

Subnitrate of bismuth was once extensively employed as a cosmetic, but is said to injure the skin, rendering it yellow and leather-like. It has been used in medicine.

The other salts of bismuth present few points of interest.

Bismuth is abundantly characterized by the decomposition of the nitrate by water, and by the blackening the subnitrate undergoes when exposed to the action of sulphuretted hydrogen gas.

A mixture of 8 parts of bismuth, 5 parts of lead, and three of tin, is known under the name of *fusible metal*, and is employed in taking impressions from dies, and for other purposes; it melts below 212°. The discrepancies so frequently observed between the properties of alloys and those of their constituent metals, plainly show that such substances must be looked upon as true chemical compounds, and not as mere mixtures; in the present cases the proof is complete, for the fusible metal has lately been obtained in crystals.*

URANIUM.

This metal is found in a few minerals, as *pitchblende*, and *uranite*, of which the former is the most abundant. It appears from the recent interesting researches of M. Peligot,† that the substance hitherto taken for metallic uranium, obtained by the action of hydrogen gas upon the black oxide, is not in reality the metal, but a protoxide, capable of uniting directly with acids, and, like the protoxide of manganese, not decomposable by hydrogen at a red-heat. The metal itself can be obtained only by the intervention of potassium, applied in the same manner as in the preparation of magnesium. It is described as a black coherent powder, or a white malleable metal, according to the state of aggregation, not oxidized by air or water, but eminently combustible when exposed to heat. It unites also with great violence with chlorine and with sulphur. M. Peligot admits three distinct oxides of uranium besides two other compounds of the metal and oxygen, which he designates as suboxides.

The equivalent of uranium is 60. Its symbol is U.

PROTOXIDE OF URANIUM. UO.—This is the ancient metal; it is prepared by several processes, one of which has been already mentioned. It is a brown powder, sometimes highly crystalline. When in minute division it is pyrophoric, taking fire in the air and burning to black oxide. It forms with acids a series of green salts. A corresponding chloride exists which forms dark green octahedral crystals, highly deliquescent and soluble in water. M. Peligot attributes a very extraordinary double function to this substance, namely, that of acting as a protoxide and forming salts with acids, and that of combining with chlorine or oxygen after the fashion of an elementary body.

DEUTOXIDE OF URANIUM; BLACK OXIDE. U_4O_5, or $2UO+U_2O_3$.—The black oxide, formerly considered as protoxide, is produced when both protoxide and peroxide are strongly heated in the air, the former gaining, and the latter losing, a certain quantity of oxygen. It forms no salts, but is resolved by solution in acids into protoxide and peroxide.

PEROXIDE OF URANIUM. U_2O_3.—The peroxide is best known and most important of the three; it forms a number of extremely beautiful yellow salts.

* Annalen der Chemie und Pharmacie, xliv. p. 275.

† Ann. Chim. et Phys., 3d Series, v. p. 5.

When caustic alkali is added to a solution of pernitrate of uranium, a yellow precipitate of hydrated oxide falls, which retains a portion of the precipitant. The hydrate cannot be exposed to a heat sufficient to expel the water without a commencement of decomposition.

NITRATE OF PEROXIDE OF URANIUM. U_2O_3, NO_5+6HO; or $(U_2O_2) O, NO_5 +6HO$; U_2O_2 being the supposed *quasi metal*. The pernitrate is the starting-point in the preparation of all the compounds of uranium; it may be prepared from pitchblende by dissolving the pulverized mineral in nitric acid, evaporating to dryness, adding water and filtering; the liquid furnishes by due evaporation crystals of nitrate of uranium, which are purified by a repetition of the process, and, lastly, dissolved in ether. This latter solution yields the pure nitrate.

The green salts of uranium are peroxidized by boiling with nitric acid.

A yellow precipitate with caustic alkalis, convertible by heat into black oxide; a brown precipitate with sulphuret of ammonium; and none at all with sulphuretted hydrogen gas, sufficiently characterize the salts of peroxide of uranium. A solution suspected to contain protoxide, may be boiled with a little nitric acid, and then examined.

The only application of uranium is that to enamel-pigment and the staining of glass; the deutoxide giving a fine black color, and the peroxide a delicate yellow.

COPPER.

Copper is a metal of great value in the arts of life; it sometimes occurs in the metallic state, crystallized in octahedrons, but is more abundant in the condition of red oxide, and in that of sulphuret combined with sulphuret of iron, or *yellow copper ore*. Large quantities of the latter substance are annually obtained from the Cornish mines and taken to South Wales for reduction, which is effected by a somewhat complex process. The principle of this may, however, be easily made intelligible. The ore is roasted in a reverberatory furnace, by which much of the sulphuret of iron is converted into oxide, while the sulphuret of copper remains unaltered. The product of this operation is then strongly heated with siliceous sand; the latter combines with the oxide of iron to a fusible *slag*, and separates from the heavier copper-compound. When the iron has, by a repetition of these processes, been got rid of, the sulphuret of copper begins to decompose in the flame-furnace, losing its sulphur and absorbing oxygen; the temperature is then raised sufficiently to reduce the oxide thus produced, by the aid of carbonaceous matter. The last part of the operation consists in thrusting into the melted metal a pole of birch-wood, the object of which is probably to reduce a little remaining oxide by the combustible gases thus generated.

Copper has a well known yellowish-red color, a specific gravity of 8·96, and is very malleable and ductile; it is an excellent conductor of heat and electricity; it melts at a bright red heat, and seems to be a little volatile at a very high temperature. Copper undergoes no change in dry air; exposed to a moist atmosphere, it becomes covered with a strongly-adherent green crust, consisting in a great measure of carbonate. Heated to redness in the air, it is quickly oxidized, becoming covered with a black scale. Dilute sulphuric and hydrochloric acids scarcely act upon copper; boiling oil of vitriol attacks it with evolution of sulphurous acid; nitric acid, even dilute, dissolves it

readily. Two oxides are known which form salts; a third, or superoxide, is said to exist.

The equivalent of copper is 31·65; its symbol, Cu.

Protoxide of copper; black oxide. CuO.—This is the base of the ordinary blue and green salts. It is prepared by calcining metallic copper at a red heat, with full exposure to air, or more conveniently, by heating to redness the nitrate, which suffers complete decomposition. When a salt of this oxide is mixed with caustic alkali in excess, a bulky pale blue precipitate of hydrated oxide falls, which, when the whole is raised to the boiling point, becomes converted into a heavy dark brown powder; this also is anhydrous oxide of copper, the hydrate suffering decomposition, even in contact with water. The oxide prepared at a high temperature is perfectly black and very dense; it is soluble in acids, and forms a series of very important salts, being isomorphous with magnesia.

Suboxide of copper; red oxide. Cu_2O.—The suboxide may be obtained by heating in a covered crucible a mixture of 5 parts of black oxide and 4 parts of fine copper filings; or by adding grape-sugar to a solution of sulphate of copper, and then putting in an excess of caustic potash; the blue solution, heated to ebullition, is reduced by the sugar, and deposits suboxide. It often occurs in beautifully transparent ruby-red crystals, associated with other ores of copper, and can be obtained in this state by artificial means. This substance forms colorless salts with acids, which are exceedingly unstable, and tend to absorb oxygen. The suboxide communicates to glass a magnificent red tint, while that given by the protoxide is green.

Sulphate of copper; blue vitriol. CuO, SO_3+5HO.—This beautiful salt is prepared by dissolving oxide of copper in sulphuric acid, or, at less expense, by oxidizing the sulphuret. It forms large blue crystals, soluble in 4 parts of cold and 2 of boiling water; by heat it is rendered anhydrous and nearly white, and by a very high temperature, decomposed. Sulphate of copper combines with the sulphates of potash and of ammonia, forming pale blue salts which contain 6 equivalents of water, and also with *ammonia*, generating a remarkable compound of deep blue color, capable of crystallizing.

Nitrate of copper. CuO, NO_5+3HO.—The nitrate is easily made by dissolving the metal in nitric acid; it forms deep-blue crystals, very soluble and deliquescent. It is highly corrosive. An insoluble subnitrate is known; it is green. Nitrate of copper also combines with ammonia.

Carbonates of copper.—When carbonate of soda is added in excess to a solution of sulphate of copper, the precipitate is at first pale blue and flocculent, but by warming it becomes sandy, and assumes a green tint; in this state it contains CuO, CO_2+CuO, HO. This substance is prepared as a pigment. The beautiful mineral *malachite*, has a similar composition. Another natural compound, not yet artificially imitated, occurs in large transparent crystals of the most intense blue; it contains $2CuO,CO_2+CuO,HO$. *Verditer*, made by decomposing nitrate of copper by chalk, is said, however, to have a somewhat similar composition.

Chloride of copper. $CuCl+2HO$.—The chloride is most easily prepared by dissolving the black oxide in hydrochloric acid, and concentrating the green solution thence resulting. It forms green crystals, very soluble in water and in alcohol; it colors the flame of the latter green. When gently heated, it parts with its water of crystallization and becomes yellowish brown; at a high temperature it loses half its chlorine and becomes converted into the subchloride. The latter is a white fusible substance, but little soluble in water, and prone to oxidation; it is formed when copper filings or copper leaf are put into chlorine gas.

Arsenite of copper; Scheele's green. This is prepared by mixing solu-

tions of sulphate of copper and arsenite of potash; it falls as a bright green insoluble powder. This compound is chiefly interesting in relation to the detection of arsenic.

The characters of the proto-salts of copper are well marked.

Caustic potash gives a pale blue precipitate of hydrate, becoming blackish-brown on boiling.

Ammonia also throws down the hydrate, but when in excess, re-dissolves it, yielding an intense purplish-blue solution.

Carbonates of potash and soda give pale blue precipitates, insoluble in excess.

Carbonate of ammonia, the same, but soluble with deep blue color.

Ferrocyanide of potassium gives a fine red-brown precipitate of ferrocyanide of copper.

Sulphuretted hydrogen and sulphuret of ammonium afford black sulphuret of copper.

The alloys of copper are of great importance. *Brass* consists of copper alloyed with from 28 to 34 per cent. of zinc; the latter may be added directly to the melted copper, or granulated copper may be heated with calamine and charcoal powder, as in the old process. *Gun-metal*, a most trust-worthy and valuable alloy, consists of 90 parts copper and 10 tin. *Bell* and *speculum metal* contain a still larger proportion of tin; these are brittle, especially that last-named. A good bronze for statues is made of 91 parts copper, 2 parts tin, 6 parts zinc, and 1 part lead. The *brass* of the ancients is an alloy of copper with tin.

LEAD.

This abundant and useful metal is altogether obtained from the native sulphuret, or *galena*, no other lead ore being found in quantity. The reduction is effected in a reverberatory furnace, into which the crushed lead ore is introduced and roasted for some time at a dull red-heat, by which much of the sulphuret becomes changed by oxidation to sulphate. The contents of the furnace are then thoroughly mixed, and the temperature raised, when the sulphate and sulphuret react upon each other, producing sulphurous acid and metallic lead.*

Lead is a soft bluish metal, possessing very little elasticity; its specific gravity is 11·45. It may be easily rolled out into plates, or drawn into coarse wire, but has a very trifling degree of strength. Lead melts at 610° or a little above, and at a white heat boils and volatilizes. By slow cooling it may be obtained in octahedral crystals. In moist air this metal becomes coated with a film of gray matter, thought to be suboxide, and when exposed to the atmosphere in a melted state, it rapidly absorbs oxygen. Dilute acids, with the exception of nitric, act but slowly upon lead. Chemists are familiar with four oxides of lead, only one of which possesses basic properties.

The equivalent of lead is 103·56; its symbol is Pb.

* Sulphate of lead . . .	Oxide of lead . .	Lead	Free.
		Oxygen	Sulphurous acid.
	Sulphuric acid . .	Sulphur	
		3 Oxygen	
Sulphuret of lead . .		Sulphur	
		Lead	Free.

PROTOXIDE; LITHARGE; MASSICOT. PbO.—This is the product of the direct oxidation of the metal. It is most conveniently prepared by heating the carbonate to dull redness; common *litharge* is impure protoxide which has undergone fusion. Protoxide of lead has a delicate straw-yellow color, is very heavy, and slightly soluble in water, giving an alkaline liquid. At a red-heat it melts, and tends to crystallize on cooling. In a melted state it attacks and dissolves siliceous matter with astonishing facility, often penetrating an earthen crucible in a few minutes. It is easily reduced when heated with organic substances of any kind containing carbon or hydrogen. Protoxide of lead forms a large class of salts, which are colorless if the acid itself be not colored.

RED OXIDE; RED LEAD. Pb_3O_4, or $2PbO+PbO_2$.—The composition of this substance is not very constant; it is prepared by exposing for a long time to the air, at a very faint red heat, protoxide of lead which has not been fused; it is a brilliant red and extremely heavy powder, decomposed with evolution of oxygen by a strong heat, and converted into a mixture of protoxide and peroxide by acids. It is used as a cheap substitute for vermilion.

PEROXIDE OF LEAD: PUCE OR BROWN OXIDE. PbO_2.—This compound is obtained without difficulty by digesting red lead in dilute nitric acid, when nitrate of protoxide is dissolved out and insoluble peroxide left behind in the form of a deep brown powder. The peroxide is decomposed by a red heat, yielding up one-half of its oxygen. Hydrochloric acid converts it into chloride of lead with disengagement of chlorine; hot oil of vitriol forms with it sulphate of lead, and liberates oxygen; and solution of ammonia gives nitrate of lead and water. The peroxide is very useful in separating sulphurous acid from certain gaseous mixtures, sulphate of lead being then produced.

SUBOXIDE OF LEAD. Pb_2O.—When oxalate of lead is heated to dull redness in a retort a gray pulverulent substance is left, which is resolved by acids into protoxide of lead and metal. It absorbs oxygen with great rapidity when heated, and even when simply moistened with water and exposed to the air.

NITRATE OF LEAD.—PbO,NO_5.—The nitrate may be obtained by dissolving carbonate of lead in nitric acid, or by acting directly upon the metal by the same agent with the aid of heat; it is, as already noticed, a by-product in the preparation of the peroxide. It crystallizes in anhydrous octahedrons, which are usually milk-white and opaque: it dissolves in 7½ parts of cold water, and is decomposed by heat, yielding pure protoxide of lead, nitrous acid, and oxygen. When a solution of this salt is boiled with an additional quantity of oxide of lead, a portion of the latter is dissolved, and a basic, or subnitrate generated, which may be had in crystals. Carbonic acid separates this excess of oxide in the form of a white compound of carbonate and hydrate of lead.

CARBONATE OF LEAD; WHITE LEAD. PbO,CO_2.—Carbonate of lead is sometimes found beautifully crystallized in long white needles, accompanying other metallic ores. It may be prepared artificially by precipitating a solution of the nitrate or acetate by an alkaline carbonate; it is also manufactured to an immense extent by other means for the use of the painter. Pure carbonate of lead is a soft, white powder, of great specific gravity, insoluble in water, but easily dissolved by dilute nitric or acetic acid.

Of the many methods put in practice, or proposed, for making white lead, the two following are the most important and interesting:—One of these consists in forming subnitrate or subacetate of lead by boiling finely-powdered litharge with the neutral salt. This solution is then brought into contact with carbonic acid gas; all the excess of oxide previously taken up by the neutral salt is at once precipitated as white lead. The solution strained or pressed from the later is again boiled with litharge, and treated with carbonic acid, these processes being susceptible of indefinite repetition, when the

little loss of neutral salt left in the precipitates, is compensated. The second, and by far the more ancient method, is rather more complex, and at first sight not very intelligible. A great number of earthen jars are prepared, into each of which are poured a few ounces of crude vinegar; a roll of sheet lead is then introduced in such a manner that it shall neither touch the vinegar nor project above the top of the jar. The vessels are next arranged in a large building, side by side, upon a layer of stable manure, or, still better, spent tan, and closely covered with boards. A second layer of tan is spread upon the top of the latter, and then a second series of pots; these are in turn covered with boards and decomposing bark, and in this manner a pile of many alternations is constructed. After the lapse of a considerable time the pile is taken down and the sheets of lead removed and carefully unrolled; they are then found to be in great part converted into carbonate, which merely requires washing and grinding to be fit for use. The theory of this curious process is generally explained by supposing the vapor of vinegar raised by the high temperature of the fermenting heat merely to act as a carrier between the carbonic acid, evolved from the tan, and the oxide of lead formed under the influence of the acid vapor, a neutral acetate, a subacetate, and a carbonate being produced in succession, the action gradually traveling from the surface inwards. The quantity of acetic acid used is, in relation to the lead, quite trifling, and cannot directly contribute to the production of carbonate. A preference is still given to the product of this old mode of manufacture on account of its superiority of opacity, or *body*, over that obtained by precipitation. Commercial white lead, however prepared, always contains a certain proportion of hydrate.

When clean metallic lead is put into pure water, and exposed to the atmosphere, a white, crystalline, scaly powder begins to show itself in a few hours, and very rapidly increases in quantity. This substance is due to the action of the carbonic acid dissolved in the water; it consists of carbonate in combination with hydrate. When common river or spring water is substituted for the pure liquid, this effect is scarcely observable, the little sulphate, almost invariably present, causing the deposition of a very thin but closely-adherent film of sulphate of lead upon the surface of the metal, which protects it from further action. It is on this account that leaden cisterns are used with impunity, at least in most cases, for holding water; if the latter were pure, it would be speedily contaminated with lead, and the cistern be soon destroyed.

Chloride of lead.—PbCl.—This salt is prepared by mixing strong solutions of acetate of lead and chloride of sodium; or by dissolving litharge in boiling dilute hydrochloric acid, and setting aside the filtered solution to cool. Chloride of lead crystallizes in brilliant, colorless needles, which require 135 parts of cold water for solution. It is anhydrous; it melts when heated, and solidifies on cooling to a horn-like substance.

Iodide of lead.—PbI.—The iodide of lead separates as a brilliant yellow precipitate when a soluble salt of lead is mixed with iodide of potassium. This compound dissolves in boiling water, yielding a *colorless* solution which deposits the iodide on cooling in splendid golden-yellow scales.

The soluble salts of lead thus behave with re-agents:—

Caustic potash and soda precipitate a white hydrate, freely soluble in excess.

Ammonia gives a similar white precipitate, not soluble in excess.*

* Ammonia gives no immediate precipitate with the acetate.

The carbonates of potash, soda, and ammonia precipitate carbonate of lead, insoluble in excess.

Sulphuric acid, or a sulphate, causes a white precipitate of sulphate of lead insoluble in nitric acid.

Sulphuretted hydrogen and sulphuret of ammonium throw down black sulphuret of lead.

An alloy of 2 parts of lead and 1 of tin constitutes *plumbers' solder;* these proportions reversed give a more fusible compound called *fine solder.* The lead employed in the manufacture of shot is combined with a little arsenic.

CERIUM AND LANTANUM.

The oxides of these very rare metals are found associated in the Swedish mineral *cerite;* the properties of the metals themselves may be said to be almost unknown. M. Vauquelin succeeded in obtaining what was supposed to be metallic cerium, in the form of minute buttons or globules of a hard brittle white metal, which resisted the action of nitric acid, but was attacked by aqua regia. Lantanum is of more recent discovery, the oxide having, it seems, been confounded with that of cerium.

The equivalent of cerium has been represented by the number 45·98; its symbol is Ce.

Two oxides of cerium have been described, viz.: the *protoxide,* CeO, a white insoluble powder having strongly basic properties, and a *sesquioxide,* C_2O_3, which has a fawn-red color, and is feebly basic. There are two corresponding chlorides, and a sulphuret.

The oxide of lantanum has a red color, but forms a white hydrate; its basic powers are very energetic.

Mosander has quite recently announced the discovery in the ore of cerium of a third metal, to which he gives the name of *didym* or *didymium.* The history of all three substances is yet very imperfect and incomplete.*

* See Phil. Mag., October, 1843.

SECTION V.

OXIDABLE METALS PROPER, WHOSE OXIDES FORM WEAK BASES OR ACIDS.

CHROMIUM.

CHROMIUM is found in the state of oxide, in combination with oxide of iron, in some abundance in the Shetland Islands, and elsewhere; as chromate of lead, it constitutes a very beautiful mineral, from which it was first obtained. The metal itself is got in a half-fused condition by mixing the oxide with $\frac{1}{5}$th of its weight of charcoal powder, enclosing the mixture in a crucible lined with charcoal, and then subjecting it to the very highest heat of a powerful furnace. It is hard, grayish-white, and brittle; of 5·9 specific gravity, and exceedingly difficult of fusion. Chromium is but little oxidable, being scarcely attacked by the most powerful acids; it forms two compounds with oxygen.

The equivalent of chromium is 28·14; its symbol is Cr.

OXIDE OF CHROMIUM. Cr_2O_3.—When chromate of mercury, prepared by mixing solutions of subnitrate of mercury and of chromate or bichromate of potash, is exposed to a red heat, it is decomposed, pure oxide of chromium, having a fine green color, remaining. In this the oxide is, like alumina after ignition, insoluble in acids. The hydrate may be had by boiling a somewhat dilute solution of bichromate of potash, strongly acidulated by hydrochloric acid, with small successive portions of sugar; carbonic acid escapes, and the chromic acid of the salt becomes converted into chloride of chromium, the color of the liquid changing from red to deep green. A slight excess of ammonia precipitates the hydrate from this solution. It has a pale purplish-green color, which becomes full green on ignition. Anhydrous oxide in a beautifully crystalline condition may be prepared by heating to full redness, in an earthen crucible, bichromate of potash. One-half of the acid suffers decomposition, oxygen being disengaged, and oxide of chromium left. The melted mass is then treated with water, which dissolves out neutral chromate of potash, and the oxide is, lastly, washed and dried. Oxide of chromium communicates a fine green tint to glass, and is used in enamel-painting.

The oxide of chromium is a feeble base, resembling, and isomorphous with, peroxide of iron and alumina; the salts it forms have a green or purple color, and are said to be poisonous.

SULPHATE OF CHROMIUM is readily obtained by dissolving the hydrated oxide in sulphuric acid. It unites with the sulphates of potash and of ammonia, giving rise to magnificent salts, which crystallize in regular octahedrons of a deep claret-color, and have a constitution resembling that of common alum, the alumina being replaced by oxide of chromium. There is some little difficulty in preparing chromium-alum, as the solution cannot be heated to any extent without decomposition; the color changes to green, and sulphate of potash crystallizes out.

CHLORIDE OF CHROMIUM. Cr_2Cl_3.—This is prepared either by passing chlorine over a mixture of oxide of chromium and charcoal, heated to redness in a porcelain tube, or by evaporating to dryness, the solution of hy-

drated oxide of chromium in hydrochloric acid, and exposing the residue to moderate heat. It is a slightly volatile, peach-blossom colored, crystalline substance, soluble with difficulty in water, giving a green solution, which, when evaporated to dryness, leaves a green powder containing 3 equivalents of water.

The salts of the oxide of chromium are easily recognized.

Caustic alkalis precipitate the hydrated oxide, easily soluble in excess.

Ammonia, the same, but nearly insoluble.

Carbonates of potash, soda, and ammonia throw down a green precipitate of carbonate and hydrate, slightly soluble in a large excess.

Sulphuretted hydrogen causes no change.

Sulphuret of ammonium precipitates the hydrate of the oxide.

CHROMIC ACID. CrO_3.—Whenever oxide of chromium is strongly heated with an alkali, in contact with air, oxygen is absorbed and chromic acid generated. Chromic acid may be obtained *nearly* pure, and in a state of great beauty, by the following simple process:—100 measures of a cold saturated solution of bichromate of potash are mixed with 150 measures of oil of vitriol, and the whole suffered to cool; the chromic acid crystallizes in brilliant crimson-red prisms. The mother-liquor is poured off, and the crystals placed upon a tile to drain, being closely covered by a glass or bell-jar.* Chromic acid is very deliquescent and soluble in water; the solution is instantly reduced by contact with organic matter.

Chromate of potash. KO, CrO_3.—This is the source of all the preparations of chromium; it is made directly from the native *chrome-iron ore*, which is a compound of the oxide of chromium and protoxide of iron, analogous to *magnetic iron ore*, by calcination with nitre or with carbonate of potash, the stone being reduced to powder, and heated for a long time with the alkali in a reverberatory furnace. The product, when treated with water, yields a yellow solution, which by evaporation deposits anhydrous crystals of the same color, isomorphous with sulphate of potash. Chromate of potash has a cool, bitter, and disagreeable taste, and dissolves in 2 parts of water at 60°.

Bichromate of potash. KO, $2CrO_3$.—When sulphuric acid is added to the preceding salt in moderate quantity, one-half of the base is removed, and the neutral chromate converted into bichromate. The new salt, of which immense quantities are manufactured for use in the arts, crystallizes by slow evaporation in beautiful red tabular crystals, derived from an oblique rhombic prism. It melts when heated, and is soluble in 10 parts of water, and the solution has an acid reaction.

Chromate of lead. PbO, CrO_3.—On mixing solution of chromate or bichromate of potash with nitrate of acetate of lead, a brilliant yellow precipitate falls, which is the compound in question; it is the *chrome-yellow* of the painter. When this compound is boiled with lime-water, one-half of the acid is withdrawn and a subchromate of an orange-red color left. The subchromate is also formed by adding chromate of lead to fused nitre, and afterwards dissolving out the soluble salts by water; the product is crystalline, and rivals vermilion in beauty of tint. The yellow and orange chrome colors are fixed upon cloth by the alternate application of the two solutions, and in the latter case by passing the dyed stuff through a bath of boiling lime-water.

Chromate of silver. AgO, CrO_3.—This salt precipitates as a reddish-brown powder when solutions of chromate of potash and nitrate of silver are mixed. It dissolves in hot dilute nitric acid, and separates on cooling, in small ruby-

* Mr. Warington; Proceedings of Chem. Soc., i. p. 18.

red platy crystals. The chromates of baryta, zinc, and mercury are insoluble; the first three are yellow, the last is brick-red.

A salt of chromic acid is at once recognized by its behavior with solutions of baryta and lead; and also by its color, and capability of furnishing, by deoxidation, the green oxide of chromium.

Chloro-chromic acid. CrO_2+Cl.—3 parts of bichromate of potash and 3½ parts of common salt are intimately mixed and introduced into a small glass retort; 9 parts of oil of vitriol are then added, and heat applied as long as dense red vapors arise. The product is a heavy deep-red liquid resembling bromine; it is decomposed by water, with production of chromic and hydrochloric acids.

TIN.

This valuable metal occurs in the state of oxide, and more rarely as sulphuret; the principal tin-mines are those of the Ertzgebirge in Saxony and Bohemia, Malacca, and more especially Cornwall. In Cornwall the tin-stone is found as a constituent of metal-bearing veins, associated with copper ore, in granite and slate rocks; and as an alluvial deposit, mixed with rounded pebbles, in the beds of several small rivers. The first variety is called *mine-* and the second *stream-tin.* Oxide of tin is also found disseminated through the rock itself in small crystals.

To prepare the ore for reduction, it is stamped to powder, washed, to separate as much as possible of the earthy matter, and roasted to expel sulphur and arsenic; it is then strongly heated with coal, and the metal thus obtained cast into large blocks, which, after being assayed, receive the stamp of the Duchy. Two varieties of commercial tin are known, called *grain* and *bar-tin;* the first is the best; it is prepared from the stream ore.

Pure tin has a white color, approaching to that of silver; it is soft and malleable, and when beat or twisted emits a peculiar crackling sound; it has a density of 7·3 and melts at 442° F. Tin is but little acted upon by air and water, even conjointly; when heated above its melting point, it oxidizes rapidly, becoming converted into a whitish powder, used in the arts for polishing, under the name of *putty powder.* The metal is easily attacked and dissolved by hydrochloric acid, with evolution of hydrogen; nitric acid acts with great energy, converting it into a white hydrate of the peroxide. There are two well-marked oxides of tin, which act as feeble bases or acids, according to circumstances, and a third, which has been less studied.

The equivalent of tin is 58·82; its symbol is Sn.

Protoxide of tin. SnO.—When solution of protochloride of tin is mixed with carbonate of potash, a white hydrate of the protoxide falls, the carbonic acid being at the same time extricated. When this is carefully washed, dried, and heated in an atmosphere of carbonic acid, it loses water and changes to a dense black pwder, whioch is permanent in the air, but takes fire on the approach of a red-hot body, and burns like tinder, producing peroxide. The hydrate is freely soluble in caustic potash; the solution decomposes by keeping into metallic tin and peroxide.

Sesquioxide of tin. Sn_2O_3.—The sesquioxide is produced by the action of hydrated peroxide of iron upon protochloride of tin; it is a grayish, slimy substance, soluble in hydrochloric acid and in ammonia. This oxide has been but little examined.

PEROXIDE OF TIN. SnO_2.—This substance is obtained in two different states, having properties altogether dissimilar. When perchloride of tin is precipitated by an alkali, a white bulky hydrate appears, which is freely soluble in acids. If, on the other hand, the bichloride be boiled with excess of nitric acid, or if that acid be made to act directly on metallic tin, a white substance is produced, which refuses altogether to dissolve in acids, and possesses properties differing in other respects from those of the first modification. Both these varieties of peroxide of tin have the same composition, and when ignited, leave the pure peroxide of a pale lemon-yellow tint. Both dissolve in caustic alkali, and are precipitated with unchanged properties by an acid. The two hydrates redden litmus paper.

PROTOCHLORIDE OF TIN. SnCl.—The protochloride is easily made by dissolving metallic tin in hot hydrochloric acid. It crystallizes in needles containing 3 equivalents of water, which are freely soluble in a small quantity of the liquid, but are apt to be decomposed in part when put into a large mass, unless hydrochloric acid in excess be present. The anhydrous chloride may be obtained by distilling a mixture of calomel and powdered tin, prepared by agitating the melted metal in a wooden box until it solidifies. The chloride is a gray, resinous-looking substance, fusible below redness, and volatile at a high temperature. Solution of protochloride of tin is employed as a de-oxidizing agent; it reduces the salts of mercury and other metals of the same class.

PERCHLORIDE, OR BICHLORIDE OF TIN. $SnCl_2$.—This is an old and very curious compound, formerly called *fuming liquor of Libavius*. It is made by exposing metallic tin to the action of chlorine, or more conveniently, by distilling a mixture of 1 part of powdered tin, and 5 parts of corrosive sublimate. The bichloride is a thin, colorless, mobile liquid; it boils at 248°, and yields a colorless invisible vapor. It fumes in the air, and when mixed with a third part of water, solidifies to a crystalline mass. The solution of bichloride is much employed by the dyer as a *mordant;* it is commonly prepared by dissolving metallic tin in a mixture of hydrochloric and nitric acids, care being taken to avoid too great elevation of temperature.

SULPHURETS OF TIN. *Protosulphuret*, SnS, is prepared by fusing tin with excess of sulphur, and strongly heating the product. It is a lead-gray, brittle substance, fusible by a red heat, and soluble with evolution of sulphuretted hydrogen in hot hydrochloric acid. A *sesquisulphuret* may be formed by gently heating the above compound with a third of its weight of sulphur; it is yellowish-gray and easily decomposed by heat. *Bisulphuret*, SnS_2, or *Mosaic gold*, is prepared by exposing to a low red heat, in a glass flask, a mixture of 12 parts of tin, 6 of mercury, 6 of sal-ammoniac, and 7 of flowers of sulphur. Sal-ammoniac, cinnabar, and protochloride of tin sublime, while the bisulphuret remains at the bottom of the vessel in the form of brilliant gold-colored scales; it is used as a substitute for gold-powder.

Salts of tin are thus distinguished:—

Protoxide.

Caustic alkalis; white hydrate, soluble in excess.	
Ammonia; carbonates of potash, soda, and ammonia	White hydrate, insoluble in excess.
Sulphuretted hydrogen Sulphuret of ammonium	Black precipitate of protosulphuret.

Peroxide.

Caustic alkalis; white hydrate, soluble in excess.
Ammonia; white hydrate, slightly soluble in excess.
Alkaline carbonates; white hydrate, slightly soluble in excess.
Carbonate of ammonia; white hydrate, insoluble.
Sulphuretted hydrogen; yellow precipitate of sulphuret.
Sulphuret of ammonium; the same, soluble in excess.

Chloride of gold, added to a dilute solution of protochloride of tin, gives rise to a brownish-purple precipitate, called *purple of Cassius*, very characteristic, whose nature is not thoroughly understood; it is supposed to be a combination of oxide of gold and sesquioxide of tin, in which the latter acts as an acid, or AuO, Sn_2O_3. Heat resolves it into a mixture of metallic gold and peroxide of tin. Purple of Cassius is employed in enamel-painting.

The useful applications of tin are very numerous. *Tinned plate* consists of iron superficially alloyed with this metal; *pewter*, of the best kind, is chiefly tin, hardened by the admixture of a little antimony, &c. Cooking vessels of copper are usually tinned in the interior.

TUNGSTEN.

Tungsten is found in the mineral *wolfram*, tolerably abundant in Cornwall; a native tungstate of lime is also occasionally met with. Metallic tungsten is obtained in the state of a dark gray powder, by strongly heating tungstic acid in a stream of hydrogen, but requires for fusion an exceedingly high temperature. It is a white metal, very hard and brittle; it has a density of 17·4. Heated to redness in the air, it takes fire, and reproduces tungstic acid.

The equivalent of tungsten is 94·64; its symbol is W. (wolframium.)

Oxide of tungsten. WO_2.—This is most easily prepared by exposing tungstic acid to hydrogen, at a temperature which does not exceed dull redness. It is a brown powder, sometimes assuming a crystalline appearance and an imperfect metallic lustre. It takes fire when heated in the air, and burns, like the metal itself, to tungstic acid. The oxide forms no salts with acids.

Tungstic acid. WO_3.—When tungstate of lime can be obtained, simple digestion in hot nitric acid is sufficient to remove the base, and liberate the tungstic acid in a state of tolerable purity; its extraction from wolfram, which contains tungstic acid or oxide of tungsten in association with the oxides of iron and manganese, is more difficult. Tungstic acid is a yellow powder, insoluble in water, and freely dissolved by caustic alkalis. When strongly ignited in the open air, it assumes a greenish tint.

Two chlorides and two sulphurets of tungsten are known to exist.

MOLYBDENUM.

Metallic molybdenum is obtained by exposing molybdic acid in a charcoal-lined crucible, to the most intense heat that can be obtained. It is a white, brittle, and exceedingly infusible metal, having a density of 8·6, and oxidizing, when heated in the air, to molybdic acid.

The equivalent of molybdenum is 47·88; its symbol is Mo.

Protoxide of molybdenum. MoO.—Molybdate of potash is mixed with excess of hydrochloric acid, by which the molybdic acid first precipitated is re-dissolved; into this acid solution zinc is put; a mixture of chloride of zinc

and protochloride of molybdenum results. A large quantity of caustic potash is then added, which precipitates a black hydrate of the protoxide of molybdenum, and retains in solution the oxide of zinc. The freshly precipitated protoxide is soluble in acids, and in carbonate of ammonia; when heated in the air, it burns to binoxide.

BINOXIDE OF MOLYBDENUM. MoO_2.—This is obtained in the anhydrous condition by heating molybdate of soda with sal-ammoniac, the molybdic acid being reduced to binoxide by the hydrogen of the ammoniacal salt; or, in a hydrated condition, by digesting metallic copper in a solution of molybdic acid, until the liquid assumes a red color, and then adding a large excess of ammonia. The anhydrous binoxide is deep brown, and insoluble in acids, the hydrate resembles hydrate of the peroxide of iron, and dissolves in acids, yielding red solutions. It is converted into molybdic acid by strong nitric acid.

MOLYBDIC ACID, MoO_3.—The native sulphuret of molybdenum is roasted, at a red heat, in an open vessel, and the impure molybdic acid thence resulting dissolved in ammonia. The filtered solution is evaporated to dryness, the salt taken up by water, and purified by crystallization. It is, lastly, decomposed by heat, and the ammonia expelled. Molybdic acid is a yellow powder, fusible at a red heat, and slightly soluble in water. It is dissolved with ease by the alkalis. Three chlorides, and as many sulphurets of molybdenum, are described.

VANADIUM.

Vanadium is found, in small quantity, in one of the Swedish iron ores, and also as *vanadiate of lead*. The most successful process for obtaining the metal is said to be the following:—The liquid chloride of vanadium is introduced into a ball, blown in a glass tube, and dry ammoniacal gas passed over it; the latter is absorbed, and a white saline mass produced. When this is heated by the flame of a spirit-lamp, hydrochlorate of ammonia is volatilized, and metallic vanadium left behind.* It is a white, brittle substance, with perfect metallic lustre, and a very high degree of infusibility; it is neither oxidized by air or water, nor attacked by sulphuric, hydrochloric or even hydrofluoric acid; aqua regia dissolves it, yielding a deep blue solution.

The equivalent of vanadium is 68·55; its symbol is V.

PROTOXIDE OF VANADIUM. VO.—This is prepared by heating vanadic acid in contact with charcoal or hydrogen; it has a black color, and imperfect metallic lustre, conducts electricity, and is very infusible. Heated in the air, it burns to binoxide. Nitric acid produces the same effect, a blue nitrate of the binoxide being generated. It does not form salts.

BINOXIDE OF VANADIUM. VO_2.—The binoxide is obtained by heating a mixture of 10 parts protoxide of vanadium, and 12 of vanadic acid, in a vessel filled with carbonic acid gas; or by adding a slight excess of carbonate of soda to a salt of the binoxide; in the latter case it falls as a grayish-white hydrate, readily becoming brown, by absorption of oxygen. The anhydrous oxide is a black insoluble powder, convertible by heat and air into vanadic acid. It forms a series of blue salts. which have a tendency to become green, and ultimately red, by the production of vanadic acid. Binoxide of vanadium also unites with alkalis.

VANADIC ACID. VO_3.—The native vanadiate of lead is dissolved in nitric acid, and the lead and arsenic precipitated by sulphuretted hydrogen, which at the same time reduces the vanadic acid to binoxide of vanadium. The blue filtered solution is then evaporated to dryness, and the residue digested

* Turner's Chemistry, p. 579.

in ammonia, which dissolves out the vanadic acid reproduced during evaporation. Into this solution a lump of sal-ammoniac is put; as that salt dissolves, vanadiate of ammonia subsides as a white powder, beng scarcely soluble in a saturated solution of hydrochlorate of ammonia. By exposure to a temperature below redness in an open crucible, the ammonia is expelled, and vanadic acid left. It has a dark red colour, and melts even below a red-heat: water dissolves it sparingly, and acids with greater ease; the solutions easily suffer de-oxidation. It unites with bases forming a series of red or yellow salts of which those of the alkalis are soluble in water.

Chlorides of vanadium—The *bichloride* is prepared by digesting vanadic acid in hydrochloric acid, passing a stream of sulphuretted hydrogen and evaporating the whole to dryness. A brown residue is left, which yields a blue solution with water and an insoluble subsalt. The *terchloride* is a yellow liquid obtained by passing chlorine over a mixture of protoxide of vanadium and charcoal. It is converted by water into hydrochloric and vanadic acids.

Two sulphurets, corresponding to the chlorides, exist.

COLUMBIUM OR TANTALUM.

This is an exceedingly rare substance; it is found in the minerals *tantalite* and *yttro-tantalite*, and may be obtained pure by heating with potassium the double fluoride of columbium and potassium. It is a gray metal, but little acted on by the ordinary acids, and burning to columbic acid when heated in the air, or when fused with hydrate of potash.

The equivalent of columbium is 184·59; its symbol is T (tantalum).

Binoxide of columbium. TO_2.—When columbic acid is heated to whiteness in a crucible lined with charcoal, the greater part is converted into this substance. It is a dark brown powder, insoluble in acids, and easily changed by oxidation to columbic acid.

Columbic acid. TO_3.—The powdered ore is fused with three or four times its weight of carbonate of potash and the product digested with water; from this solution acids precipitate a white hydrate of the body in question. It is soluble in acids, but forms with them no definite compounds; with alkalis it yields, on the contrary, crystallizable salts.

TITANIUM.

Crystallized oxide of titanium is found in nature in the forms of *titanite* and *anatase*. The metal itself is met with occasionally in the slag adherent to the bottom of blast-furnaces in which iron ore is reduced, as small brilliant copper-colored cubes, hard enough to scratch glass, and in the highest degree infusible. They resist the action of acids but are oxidized when heated with nitre. Metallic titanium in a finely-divided state may be obtained by artificial means. There are two compounds of this substance with oxygen, viz: an oxide and an acid; very little is known respecting the former.

The equivalent of titanium is 24·29; its symbol is Ti.

Titanic acid. TiO_2.—Titanite, or titaniferous iron ore, is reduced to fine powder and fused with three parts of carbonate of potash; the product is washed with water to remove all soluble matter, and the residue dissolved in strong hydrochloric acid. On dilution with water and boiling, titanic acid is precipitated. When pure, the acid is quite white; it is, when recently precipitated, soluble in acids, but the solutions are decomposed by mere boiling. After ignition it is no longer soluble. Titanic acid on the whole very much resembles silica, and is probably often overlooked and confounded with that substance in analytical researches.

Bichloride of titanium.—This is a colorless, volatile liquid, resembling bichloride of tin; it is obtained by passing chlorine over a mixture of titanic acid and charcoal at a high temperature. It unites very violently with water.

ANTIMONY.

This important metal is found chiefly in the state of sulphuret. The ore is freed by fusion from earthy impurities, and is afterwards decomposed by heating with metallic iron or carbonate of potash, which retains the sulphur. Antimony has a bluish-white color and strong lustre; it is extremely brittle, being reduced to powder with the utmost ease. Its specific gravity is 6·8; it melts at a temperature just short of redness, and boils and volatilizes at a white heat. This metal has always a distinct crystalline, platy structure, but by particular management it may be obtained in crystals, which are rhombohedral. Antimony is not oxidized by the air at common temperatures; strongly heated, it burns with a white flame, producing oxide, which is often deposited in beautiful crystals. It is dissolved by hot hydrochloric acid, with evolution of hydrogen and production of chloride. Nitric acid oxidizes it to antimonic acid, which is insoluble in that menstruum. There are three compounds of antimony and oxygen; the first has doubtful basic properties, the two others are acids.

The equivalent of antimony is 129·04. Its symbol is Sb (stibium).

Oxide of antimony. SbO_3.—This compound may be prepared by several methods; as by burning metallic antimony at the bottom of a large red-hot crucible, in which case it is obtained in brilliant crystals; or by pouring solution of chloride of antimony into water, and digesting the resulting precipitate with a solution of carbonate of soda. The oxide thus produced is anhydrous; it is a pale buff-colored powder, fusible at a red heat, and volatile in a close vessel, but in contact with air it, at a high temperature, absorbs oxygen and becomes changed to antimonious acid. When boiled with cream of tartar (acid tartrate of potash,) it is dissolved, and the solution yields on evaporation crystals of *tartar-emetic*, which is almost the only compound of oxide of antimony with an acid which bears admixture with water without decomposition. An impure oxide for this purpose is sometimes prepared by carefully roasting the powdered sulphuret in a reverberatory furnace, and raising the heat at the end of the process so as to fuse the product; it has long been known under the name of *glass of antimony*.

Antimonious acid. SbO_4.—This is the ultimate product of the oxidation of the metal by heat and air; it is a grayish-white powder, infusible, and destitute of volatility; it is insoluble in water and in acids, except when recently precipitated. It combines with alkalis yielding solutions from which acids precipitate the hydrate; the latter reddens litmus-paper.

Antimonic acid. SbO_5.—When strong nitric acid is made to act upon metallic antimony, the metal is oxidized to its highest point, and antimonic acid produced, which is insoluble. By exposure to a heat short of redness it is rendered anhydrous, and then presents the appearance of a pale straw-colored powder, insoluble in water and acids, but dissolving in alkalis, with which it forms definite compounds. These latter when in solution are decomposed by acids, a white hydrate of antimonic acid being precipitated. Antimonic acid is decomposed by a red heat, yielding antimonious acid, with loss of oxygen.

Terchloride of antimony; butter of antimony. $SbCl_3$.—This substance is produced when sulphuretted hydrogen is prepared by the action of strong hydrochloric acid on sulphuret of antimony. The impure and highly acid solution thus obtained is put into a retort and distilled until each drop of the condensed product, on falling into the aqueous liquid of the receiver, pro-

duces a copious white precipitate. The receiver is then changed and the distillation continued. Pure chloride of antimony passes over and solidifies on cooling to a white and highly crystalline mass, from which the air requires to be carefully excluded. The same compound is formed by distilling metallic antimony in powder with $2\frac{1}{2}$ times its weight of corrosive sublimate. Chloride of antimony is very deliquescent; it dissolves in strong hydrochloric acid without decomposition, and the solution, poured into water gives rise to a white bulky precipitate, which after a short time becomes highly crystalline, and assumes a pale fawn color. This is the old *powder of Algaroth;* it is a compound of chloride and oxide of antimony. Alkaline solutions extract the chloride and leave oxide of antimony. Finely-powdered antimony thrown into chlorine gas, inflames.

A chloride of antimony, corresponding to antimonic acid, is formed by passing a stream of chlorine gas over gently heated metallic antimony: a mixture of the two chlorides results, which may be separated by distillation. The *pentachloride* is a colorless volatile liquid, which forms a crystalline compound with a small portion of water, but is decomposed by a larger quantity into antimonic and hydrochloric acids.

SULPHURET OF ANTIMONY; CRUDE ANTIMONY. SbS_3.—The native sulphuret is a lead gray, brittle substance, having a radiated, crystalline texture, and is easily fusible. It may be prepared artificially by melting together antimony and sulphur. When a solution of tartar-emetic is precipitated by sulphuretted hydrogen, a brick red precipitate falls, which is the same substance combined with a little water. If the precipitate be dried and gently heated, the water may be expelled without other change of color than a little darkening, but at a higher temperature it assumes the color and aspect of the native sulphuret. This remarkable change probably indicates a passage from the amorphous to the crystalline condition.

When powdered sulphuret of antimony is boiled in a solution of caustic potash it is dissolved, oxide of antimony and sulphuret of potassium being produced. The latter unites, with an additional quantity of sulphuret of antimony, to form a soluble sulphur salt, in which the sulphuret of potassium is the sulphur-base, and the sulphuret of antimony the sulphur-acid.

3 eq. potash {	3 eq. potassium	} 3 eq. sulphuret of potassium.
	3 eq. oxygen	
Sulphuret of antimony {	3 eq. sulphur	
	1 eq. antimony	1 eq. oxide of antimony.

The oxide of antimony separates in small crystals from the boiling solution when the latter is concentrated, and the sulphur-salt dissolves an extra proportion of sulphuret of antimony, which it again deposits on cooling as a red amorphous powder, containing a small admixture of oxide of antimony and sulphuret of potassium. This is the *kermes mineral* of the old chemists. The filtered solution mixed with an acid gives a salt of potash, suphuretted hydrogen, and precipitated sulphuret of antimony. Kermes may also be made by fusing a mixture of 5 parts sulphuret of antimony and 3 of dry carbonate of soda, boiling the mass in 80 parts of water, and filtering while hot; the compound separates on cooling.

A *pentasulphuret of antimony*, SbS_5, formerly called *sulphur auratum*, also exists; it is a sulphur-acid. 18 parts finely-powdered sulphuret of antimony, 17 parts dry carbonate of soda, 13 parts lime in the state of hydrate, and $3\frac{1}{2}$ parts sulphur, are boiled for some hours in a quantity of water; carbonate of lime, antimoniate of soda, pentasulphuret of antimony and sulphuret of sodium

are produced. The first is insoluble, and the second partially so; the two last-named bodies, on the contrary, unite to a soluble sulphur-salt, which may by evaporation be obtained in beautiful crystals. A solution of this substance, mixed with dilute sulphuric acid, furnishes sulphate of soda, sulphuretted hydrogen, and pentasulphuret of antimony, which falls as a golden-yellow flocculent precipitate.*

A compound of antimony and hydrogen exists, but has not been isolated; when zinc is put into a solution of oxide of antimony, and sulphuric acid added, the hydrogen disengaged holds antimony as it were in solution. When the gas is conducted through a red-hot glass tube of narrow dimensions, or burned with a limited supply of air, metallic antimony is deposited.

The few salts of antimony soluble in water are amply characterized by the orange or brick-red precipitate with sulphuretted hydrogen, which is soluble in solution of sulphuret of ammonium, and again precipitated by an acid.

Besides its application to medicine, antimony is of great importance in the arts of life, inasmuch as it forms with lead type-metal. This alloy expands at the moment of solidifying, and takes an exceedingly sharp impression of the mould. It is remarkable that both its constituents shrink under similar circumstances, and make very bad castings.

TELLURIUM.

This metal, or semi-metal, is of very rare occurrence; it is found in a few scarce minerals in association with silver, lead, and bismuth, apparently replacing sulphur, and is most easily extracted from the sulpho-telluret of bismuth of Chemnitz, in Hungary. The finely-powdered ore is mixed with an equal weight of dry carbonate of soda, the mixture made into a paste with oil, and heated to whiteness in a closely covered crucible. Telluret and sulphuret of sodium are produced and metallic bismuth set free. The fused mass is dissolved in water and the solution freely exposed to the air, when the sodium and sulphur oxidize to caustic soda and hyposulphite of soda, while the tellurium separates in the metallic state. Tellurium has the color and lustre of silver; by fusion and slow cooling it may be made to exhibit the form of rhombohedral crystals similar to those of antimony and arsenic. It is brittle, and a comparatively bad conductor of heat and electricity: it has a density of 6·26, melts at a little below a red heat, and volatilizes at a higher temperature. Tellurium burns when heated in the air, and is oxidized by nitric acid. Two compounds of this substance with oxygen are known, having acid properties; they much resemble the acids of arsenic.

The equivalent of tellurium is 64·14; its symbol is Te.

Tellurous acid. TeO_2.—This is obtained by burning tellurium in the air, or by heating it in fine powder with nitric acid of 1·25 specific gravity; a solution is rapidly formed, from which white anhydrous octahedral crystals of tellurous acid are deposited on standing. The acid is fusible at a red heat, and slightly volatile at a higher temperature; it is but feebly soluble in water or acids, easily dissolved by alkalis, and reduced when heated with carbon or hydrogen. A hydrate of tellurous acid is thrown down when tellurite of potash is mixed with a slight excess of nitric acid; it is a white powder, soluble to a certain extent in water, and reddens litmus.

* Mitscherlich, Lehrbuch, ii p 468.

TELLURIC ACID. TeO_3.—Equal parts of tellurous acid and carbonate of soda are fused, and the product dissolved in water; a little hydrate of soda is added, and a stream of chlorine passed through the solution. The liquid is next saturated with ammonia, and mixed with solution of chloride of barium, by which a white insoluble precipitate of tellurate of baryta is thrown down. This is washed and digested with a quarter of its weight of sulphuric acid, diluted with water. The filtered solution gives, on evaporation in the air, large crystals of telluric acid.

Telluric acid is freely, although slowly, soluble in water; it has a metallic taste, and reddens litmus paper. When the crystals are strongly heated, they lose water, and yield anhydrous acid, which is then insoluble in water, and even in a boiling alkaline liquid. At the temperature of ignition, telluric acid loses oxygen, and passes into tellurous acid. The salts of the alkalis are soluble, but do not crystallize; those of the earths are nearly, or quite insoluble.

There are two chlorides of tellurium, and also a hydruret, which closely resembles sulphuretted hydrogen.

ARSENIC.

Arsenic is sometimes found native; the largest proportion, however, is derived from the roasting of natural arseniurets of iron, nickel, and cobalt; the operation is conducted in a reverberatory furnace, and the volatile products condensed in a long and nearly horizontal chimney, or in a kind of tower of brickwork, divided into numerous chambers. The crude arsenious acid thus produced is purified by sublimation, and then heated with charcoal in a retort; the metal is reduced, and readily sublimes.

Arsenic has a steel gray color and high metallic lustre; it is crystalline and very brittle; it tarnishes in the air, but may be preserved unchanged in pure water. Its density is 5·7 to 5·9. When heated, it volatilizes without fusion, and if air be present, oxidizes to arsenious acid. The vapor has the odor of garlic. This substance combines with metals in the same manner as sulphur and phosphorus, which it resembles, especially the latter, in many respects. With oxygen it unites in two proportions, giving rise to arsenious and arsenic acids. There is no basic oxide of arsenic.

The equivalent of arsenic is 75·21; its symbol is As.

ARSENIOUS ACID; WHITE OXIDE OF ARSENIC. AsO_3.—The origin of this substance is mentioned above. It is commonly met with in the form of a heavy, white, glassy-looking substance, with smooth conchoidal fracture, which has evidently undergone fusion. When freshly prepared it is often transparent, but by keeping becomes opaque, at the same time slightly diminishing in density, and acquiring a greater degree of solubility in water. 100 parts of that liquid dissolve, at 212°, about 11·5 parts of the opaque variety; the largest portion separates, however, on cooling, leaving about 3 parts dissolved; the solution feebly reddens litmus. Cold water, agitated with powdered arsenious acid, takes up a still smaller quantity. Alkalis dissolve this substance freely, forming arsenites, which do not crystallize; it is also easily soluble in hot hydrochloric acid. The vapor of arsenious acid is colorless and inodorous; it crystallizes on solidifying in brilliant transparent octahedrons, which are very characteristic. The acid itself has a feeble, sweetish and astringent taste, and is a most fearful poison.*

* The best antidote for arsenious acid is the hydrate of the red oxide of iron. In its recently precipitated gelatinous condition, it is most active. It acts by forming an insoluble arseniate of the protoxide of iron; for the peroxide is reduced to protoxide by

ARSENIC ACID. AsO_5.—Powdered arsenious acid is dissolved in hot hydrochloric acid, and peroxidized by the addition of nitric acid, the latter being added as long as red vapors are produced; the whole is then cautiously evaporated to complete dryness. The acid thus produced is white and anhydrous. Put into water, it slowly but completely dissolves, giving a highly acid solution, which, on being evaporated to a syrupy consistence, deposits after a time, hydrated crystals of arsenic acid. When strongly heated, it is decomposed into arsenious acid and oxygen gas.

This substance is a very powerful acid, comparable with the phosphoric, which it resembles in the closest manner, forming salts strictly isomorphous with the corresponding phosphates; it is also tribasic. An arseniate of soda, $2NaO, HO, AsO_5+24HO$, undistinguishable in appearance from common phosphate of soda, may be prepared by adding the carbonate to a solution of arsenic acid, until an alkaline reaction is apparent, and then evaporating. This salt also crystallizes with 14 equivalents of water. Another arseniate, $3NaO, AsO_5+24\,HO$, is produced when carbonate of soda in excess is fused with arsenic acid, or when the preceding salt is mixed with caustic soda. A third, $NaO, 2HO, AsO_5+2HO$, is made by substituting an excess of arsenic acid for the solution of alkali. The alkaline arseniates, which contain basic water, lose the latter at a red heat, but, unlike the phosphates, recover it when again dissolved.* The salts of the alkalis are soluble in water; those of the earths, and other metallic oxides, are insoluble, but are dissolved by acids. The precipitate with nitrate of silver is highly characteristic of arsenic acid; it is reddish brown.

Three SULPHURETS OF ARSENIC are known. *Realgar*, AsS_2, occurs native; it is formed artificially, by heating arsenic or arsenious acid with a minimum of sulphur. It is a red, fusible, and volatile substance, employed by the pyrotechnist, in making *white-fire*. *Orpiment*, AsS_3, which is also a natural product of the mineral kingdom, is made by fusing arsenious acid with excess of sulphur, or by precipitating a solution of the acid by sulphuretted hydrogen. It is a golden-yellow crystalline substance, fusible and volatile by heat. Two higher sulphurets are also described, AsS_5, corresponding to arsenic acid, and AsS_9; the former is produced when sulphuretted hydrogen is transmitted through a solution of arsenic acid. It is a yellow, fusible substance, capable of sublimation. Realgar, orpiment, and pentasulphuret of arsenic, are sulphur-acids.

Arsenic unites with chlorine, iodine, &c. The *terchloride*, $AsCl_3$, is formed by distilling a mixture of 1 part of arsenic, and 6 parts of corrosive sublimate; it is a colorless, volatile liquid, decomposed by water into arsenious and hydrochloric acids. The same substance is produced, with disengagement of heat and light, when powdered arsenic is thrown into chlorine gas. The *iodide*, AsI_3, is formed by heating metallic arsenic with iodine; it is a deep-red crystalline substance, capable of sublimation. The *bromide* and *fluoride* are both liquid.

Arsenic also combines with hydrogen, forming a gaseous compound, AsHr,

losing oxygen, which, passing to the arsenious acid, forms arsenic acid. This change is represented by the following formula,

$$2\,Fe_2O_3 \text{ and } AsO_3 = 4\,FeO+AsO_5.$$

The hydrate is incapable of decomposing the arsenites. The red oxide, to act as an antidote to the arsenical salts, requires to be combined with an acid, which may separate the base, and then the arsenious acid and red oxide react on each other as above. The acetate of the red oxide is the salt used.

Magnesia has also been recommended. In the state of recently precipitated hydrate, it acts on a solution of arsenious acid, with nearly the same rapidity as the hydrated peroxide of iron. In the condition usually found in the shops, it cannot be depended on with the same certainty, having been too highly calcined.—R. B.

* Graham, Elements, p. 630.

the analogue of phosphuretted hydrogen. It is obtained pure by the action of strong hydrochloric acid on an alloy of equal parts zinc and arsenic, and is produced in greater or less proportion whenever hydrogen is set free in contact with arsenious acid. Arseniuretted hydrogen is a colorless gas, of 2·695 specific gravity, slightly soluble in water, and having the smell of garlic. It burns when kindled with a blue flame, generating arsenious acid. It is also decomposed by transmission through a red-hot tube. Many metallic solutions are precipitated by this substance. It is, when inhaled, exceedingly poisonous, even in very minute quantity.

Arsenious acid is distinguished by characters which cannot be misunderstood.

Nitrate of silver, mixed with a solution of arsenious acid in water, occasions no precipitate, or merely a faint cloud; but if a little alkali, as a drop of ammonia, be added, a yellow precipitate of arsenite of silver immediately falls. The precipitate is exceedingly soluble in excess of ammonia; that substance must therefore be added with great caution.

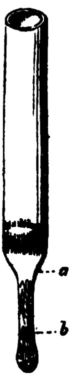
Sulphate of copper gives no precipitate with solution of arsenious acid, until the addition has been made of a little alkali, when a brilliant yellow-green precipitate (Scheele's green) falls, which also is very soluble in excess of ammonia.

Sulphuretted hydrogen passed into a solution of arsenious acid, to which a few drops of hydrochloric or sulphuric acid have been added, occasions the production of a copious bright yellow precipitate of orpiment, which is dissolved with facility by ammonia, and is re-precipitated by acids.

Solid arsenious acid, heated by the blow-pipe in a narrow glass tube with small fragments of dry charcoal, affords a sublimate of metallic arsenic in the shape of a brilliant steel-gray metallic ring. A portion of this, detached by the point of a knife and heated in a second glass tube, with access of air, yields, in its turn, a sublimate of colorless, transparent octahedral crystals of arsenious acid.

All these experiments, which *jointly* give demonstrative proof of the presence of the substance in question, may be performed, with perfect precision and certainty, upon exceedingly small quantities of material.

Fig. 141.



The detection of arsenious acid in complex mixtures containing organic matter and common salt, as beer, gruel, soup, &c., or the fluid contents of the stomach in cases of poisoning, is a very far more difficult problem, but one which is, unfortunately, often required to be solved. These organic matters interfere completely with the liquid tests, and render their indications worthless. Sometimes the difficulty may be eluded by a diligent search in the suspected liquid, and in the vessel containing it, for fragments or powder of solid arsenious acid, which, from the small degree of solubility and high density of the substance, often escape solution. If anything of the kind be found, it may be washed by decantation with a little cold water, dried, and then reduced with charcoal. For the latter purpose, a small glass tube is taken, having the figure represented in the margin; white German glass, free from lead, is to be preferred. The arsenious acid, or what is suspected to be such, is dropped to the bottom, and covered with splinters or little fragments of charcoal, the tube being filled to the shoulder. The whole is gently heated, to expel any moisture that may be present in the charcoal, and the deposited water wiped from the interior of the tube with bibulous paper. The

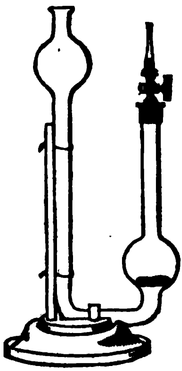
narrow part of the tube containing the charcoal, from *a* to *b*, is now heated by the blow-pipe flame; when red hot, the tube is inclined, so that the bottom also may become heated. The arsenious acid, if present, is vaporized, and reduced by the charcoal, and a ring of metallic arsenic deposited on the cool part of the tube. To complete the experiment, the tube may be melted at *a* by the point of the flame, drawn off, and closed, and the arsenic oxidized to arsenious acid, by chasing it up and down by the heat of a small spirit-lamp. A little water may afterwards be introduced, and boiled in the tube, by which the arsenious acid will be dissolved, and to this solution the tests of nitrate of silver and ammonia, sulphate of copper and ammonia, and sulphuretted hydrogen, may be applied.

When the search for solid arsenious acid fails, the liquid itself must be examined; a tolerably limpid solution must be obtained, from which the arsenic may be precipitated by sulphuretted hydrogen, and the orpiment collected, and reduced to the metallic state. It is in the first part of this operation that the chief difficulty is found; such organic mixtures refuse to filter, or filter so slowly, as to render some method of acceleration indispensable. Boiling with a little caustic potash or acetic acid will sometimes effect this object. The following is an outline of a plan, which has been found successful in a variety of cases, in which a very small quantity of arsenious acid had been purposely added to an organic mixture. Oil of vitriol, itself perfectly free from arsenic, is mixed with the suspected liquid, in the proportion of about a measured ounce to a pint, having been previously diluted with a little water, and the whole is boiled in a flask for half an hour, or until a complete separation of solid and liquid matter becomes manifest. The acid converts any starch that may be present into dextrine and sugar; it coagulates completely albuminous substances, and caseine, in the case of milk, and brings the whole in a very short time into a state in which filtration is both easy and rapid. Through the filtered solution, when cold, a current of sulphuretted hydrogen is transmitted, and the liquid is warmed, to facilitate the deposition of the sulphuret, which falls, in combination with a large quantity of organic matter, which often communicates to it a dirty color. This is collected upon a small filter, and washed. It is next transferred to a capsule, and heated with a mixture of nitric and hydrochloric acids, by which the organic impurities are in a great measure destroyed, and the arsenic oxidized to arsenic acid. The solution is evaporated to dryness, the soluble part taken up by dilute hydrochloric acid, and then the solution saturated with sulphuretted hydrogen; after some time, a sulphuret again precipitates. The liquid is warmed, and the precipitate washed by decantation, and dried. It is then mixed with *black-flux*, and heated in a small glass tube, similar to that already described, with similar precautions; a ring of reduced arsenic is obtained, which may be oxidized to arsenious acid, and further examined. The black-flux is a mixture of carbonate of potash and charcoal, obtained by calcining cream of tartar in a close crucible; the alkali is the effective agent in the reduction, the charcoal serving the purpose of preventing subsequent oxidation. A mixture of anhydrous carbonate of soda and charcoal may be substituted with advantage for the common black-flux, as it is less hygroscopic.*

Other methods of proceeding, different in principle from the foregoing, have been proposed, as that of Mr. Marsh, which is exceedingly delicate. The suspected liquid is acidulated with sulphuric acid and placed in contact with metallic zinc; the hydrogen reduces and dissolves the arsenic, if any be present. The gas is burned at a jet, and a piece of glass or porcelain held in

* See a paper by the author on the detection of arsenic. Pharmaceutical Journal, i. p. 514.

Fig. 142.



the flame, when any admixture of arseniuretted hydrogen is at once known by the production of a brilliant black metallic spot of reduced arsenic on the porcelain.

A convenient form of instrument for the purpose is that shown in the drawing; it consists of a bent tube, having two bulbs blown upon it, fitted with a stop-cock and narrow jet. Slips of zinc are put into the lower bulb, which is afterwards filled with the liquid to be examined. On replacing the stop-cock, closed, the gas collects and forces the fluid into the upper bulb, which then acts by its hydrostatic pressure and expels the gas through the jet so soon as the stop-cock is opened. It must be borne in mind that both common zinc and sulphuric acid often contain traces of arsenic.*

A slip of copper foil boiled in the poisoned liquid, previously acidulated with hydrochloric acid, withdraws the arsenic and becomes covered with a white alloy. By heating the metal in a glass tube the arsenic is expelled.

* Where the amount of arsenic present is small, it becomes necessary to take advantage of the effects of heat, and cause the gas to pass slowly through a red hot tube until all the zinc is dissolved. The reduced arsenic will be deposited on the cool part of the tube just beyond the heated portion. In all cases of using the above test, it is necessary to ascertain the purity of the zinc and acid by trial, previous to addition of the suspected liquid.—R. B.

SECTION VI.

METALS WHOSE OXIDES ARE REDUCED BY HEAT.

SILVER.

Silver is found in the metallic state, in union with sulphur, and also as chloride. Among the principal silver-mines may be mentioned those of the Hartz mountains in Germany, of Kongsberg, in Norway, and more particularly, of the Andes in both North and South America.

The greater part of the silver of commerce is extracted from ores so poor as to render any process of *smelting* or fusion inapplicable, even where fuel could be obtained; and this is often difficult to be procured; recourse, therefore, is had to another method, that of *amalgamation*, founded on the easy solubility of silver, and many other metals in metallic mercury.

The amalgamation process, as conducted in Saxony, differs somewhat from that in use in America. The ore is crushed to powder, mixed with a quantity of common salt, and roasted at a low red heat in a suitable furnace, by which treatment any sulphuret of silver it may contain is converted into chloride. The mixture of earthy matter, oxides of iron, copper, soluble salts, chloride of silver, and metallic silver, is sifted, and put into large barrels, made to revolve on axes, with a quantity of water and scraps of iron, and the whole agitated together for some time, during which the iron reduces the chloride of silver to the state of metal. A certain proportion of mercury is then introduced and the agitation repeated; the mercury dissolves out the silver, together with gold, if there be any, metallic copper, and other substances, forming a fluid amalgam easily separable from the thin mud of earthy matter by subsidence and washing. This amalgam is strained through strong linen cloth, and the solid portion exposed to heat in a kind of retort, by which the remaining mercury is volatilized, and the silver left behind in an impure condition.

A considerable quantity of silver is obtained from argentiferous galena; in fact almost every specimen of native sulphuret of lead will be found to contain traces of this metal. When the proportion rises to a certain amount, it becomes worth extracting. The ore is reduced in the usual manner, the whole of the silver remaining with the lead; the latter is then re-melted in a large vessel, and slowly allowed to cool until solidification commences. The portion which first crystallizes is nearly pure lead, the alloy with silver being *more fusible than lead itself;* by particular management this is drained away, and is found to contain nearly the whole of the silver. This rich mass is next exposed to a red heat on the shallow hearth of a furnace, while a stream of air is allowed to impinge upon its surface; oxidation takes place with great rapidity, the fused oxide or litharge being constantly swept from the metal by the blast. When the greater part of the lead has been thus removed, the residue is transferred to a *cupel* or shallow dish made of bone-ashes, and again heated; the last of the lead is now oxidized, and the oxide sinks in a melted state into the porous vessel, while the silver, almost chemically pure, and exhibiting a brilliant surface, remains behind.

Pure silver may be easily obtained. The metal is dissolved in nitric acid; if it contain copper, the solution will have a blue tint; gold will remain undissolved as a black powder. The solution is mixed with hydrochloric acid, or with common salt, and the white, insoluble, curdy precipitate of chloride of silver washed and dried. This is then mixed with about twice its weight of anhydrous carbonate of soda, and the mixture, placed in an earthen crucible, gradually raised to a temperature approaching whiteness, during which the carbonate of soda and the chloride react upon each other, carbonic acid and oxygen escape, while metallic silver and chloride of sodium result; the former fuses into a button at the bottom of the crucible, and is easily detached.

Pure silver has a most perfect white color, and a high degree of lustre; it is exceedingly malleable and ductile, and is probably the best conductor both of heat and electricity known Its specific gravity is 10·5. In hardness it lies between gold and copper. It melts at a bright red-heat, about 1873° F., according to the observations of Mr. Daniell. Silver is unalterable by air and moisture; it refuses to oxidize at any temperature, but possesses the extraordinary faculty, already noticed in an earlier part of the work, of absorbing many times its volume of oxygen when strongly heated in an atmosphere of that gas, or in common air. This oxygen is again disengaged at the moment of solidification, and gives rise to the peculiar arborescent appearance often remarked on the surface of masses or buttons of pure silver. The addition of 2 per cent. of copper is sufficient to prevent this absorption of oxygen. Silver oxidizes when heated with fusible siliceous matter, as glass, which it stains yellow or orange, from the formation of a silicate. It is little attacked by hydrochloric acid; boiling oil of vitriol converts it into sulphate with evolution of sulphurous acid, and nitric acid, even dilute and in the cold, dissolves it readily. The tarnishing of surfaces of silver exposed to the air is due to sulphuretted hydrogen, the metal having a strong attraction for sulphur. There are three oxides of silver, one of which is a powerful base isomorphous with potash, soda, and oxide of ammonia.

The equivalent of silver is 108·12; its symbol is Ag (argentum).

Suboxide of silver. Ag_2O.—When dry citrate of silver is heated to 212° in a stream of hydrogen gas, it loses oxygen and becomes dark brown. The product dissolved in water gives a dark colored solution containing free citric acid and citrate of the suboxide of silver. The suboxide is then precipitated by potash. It is a black powder, very easily decomposed, and soluble in ammonia. The solution of citrate is rendered colorless by heat, being resolved into a salt of the protoxide and metallic silver.

Protoxide of silver. AgO.—Caustic potash added to solution of nitrate of silver throws down a pale brown precipitate, which consists of protoxide of silver. It is very soluble in ammonia, and is dissolved also to a small extent by pure water; the solution is alkaline. Recently precipitated chloride of silver, boiled in a solution of caustic potash of specific gravity 1·25, is converted, according to the observation of Dr. Gregory, into oxide of silver, which in this case is black and very dense. The protoxide of silver neutralizes acids completely, and forms for the most part colorless salts. It is decomposed by a red heat, with extrication of oxygen, spongy metallic silver being left; the sun's rays also effect its decomposition to a small extent.

Peroxide of silver.—This is a black crystalline substance which forms upon the positive electrode of a voltaic arrangement employed to decompose a solution of nitrate of silver. It is reduced by heat; evolves chlorine when acted upon by hydrochloric acid; explodes when mixed with phosphorus, and struck; and decomposes solution of ammonia with great energy and rapid disengagement of nitrogen gas.

Nitrate of silver. AgO,NO_5.—The nitrate is prepared by directly dissolving silver in nitric acid and evaporating the solution to dryness, or until it is strong enough to crystallize on cooling. The crystals are colorless, transparent, anhydrous tables, soluble in an equal weight of cold, and in half that quantity of boiling water; they also dissolve in alcohol. They fuse when heated like those of nitre, and at a higher temperature, suffer decomposition; the *lunar caustic* of the surgeon is nitrate of silver which has been melted and poured into a cylindrical mould. This salt blackens when exposed to light, more particularly if organic matters of any kind be present, and is frequently employed to communicate a dark stain to the hair; it enters into the composition of the "indelible" ink used for marking linen. The black stain has been thought to be metallic silver; it may possibly be suboxide. Pure nitrate of silver may be prepared from the metal alloyed with copper; the alloy is dissolved in nitric acid, the solution evaporated to dryness, and the mixed nitrates cautiously heated to fusion. A small portion of the melted mass is removed from time to time for examination; it is dissolved in water, filtered, and ammonia added to it in excess. While any copper-salt remains undecomposed, the liquid will be blue, but when that no longer happens, the nitrate may be suffered to cool, dissolved in water, and filtered from the insoluble black oxide of copper.

Sulphate of silver. AgO,SO_3.—The sulphate may be prepared by boiling together oil of vitriol and metallic silver, or by precipitating nitrate of silver by an alkaline sulphate. It dissolves in 88 parts of boiling water, and separates in great measure in a crystalline form on cooling, having but a feeble degree of solubility at a low temperature. It forms a crystallizable compound with ammonia, freely soluble in water, containing AgO,SO_3+2NH_3.

Hyposulphate of silver, AgO,S_2O_5+2HO, is a soluble, crystallizable salt, permanent in the air. The *hyposulphite* is insoluble, white, and very prone to decomposition; it combines with the alkaline hyposulphites forming soluble compounds distinguished by an intensely sweet taste. The alkaline hyposulphites dissolve both oxide and chloride of silver, and give rise to similar salts, an oxide or chloride of the alkaline metal being at the same time formed. *Carbonate of silver* is a white insoluble substance obtained by mixing solutions of nitrate of silver and of carbonate of soda. It is blackened and decomposed by boiling.

Chloride of silver. $AgCl$.—This substance is almost invariably produced when a soluble salt of silver and a soluble chloride are mixed. It falls as a white curdy precipitate, quite insoluble in water and nitric acid, and but slightly dissolved by a large quantity of hydrochloric acid or an alkaline chloride. When heated it melts, and on cooling becomes a grayish crystalline mass, which cuts like horn; it is found native in this condition, constituting the *horn-silver* of the mineralogist. Chloride of silver is decomposed by light both in a dry and wet state, *very* slowly if pure, and quickly if organic matter be present; it is reduced also when put into water with metallic zinc or iron. It is soluble with great ease in ammonia, and in a solution of cyanide of potassium. In practical analysis the proportion of chlorine or hydrochloric acid in a compound, is always estimated by precipitation by solution of silver. The liquid is acidulated with nitric acid and an excess of nitrate of silver added; the chloride is collected on a filter, or by subsidence, washed, dried, and fused; 100 parts correspond to 24·26 of chlorine, or 25·37 of hydrochloric acid.

Iodide of silver. AgI.—The iodide is a pale yellow insoluble precipitate, produced by adding nitrate of silver to iodide of potassium; it is insoluble, or nearly so, in ammonia, and forms an exception to the silver-salts in general in this respect. The *bromide* of silver very closely resembles the chloride.

SULPHURET OF SILVER. AgS.—This is a soft, gray, and somewhat malleable substance, found native in a crystallized state, and easily produced by melting together its constituents, or by precipitating a solution of silver by sulphuretted hydrogen. It is a strong sulphur-base, and combines with the sulphurets of antimony and arsenic; examples of such compounds are found in the beautiful minerals *dark* and *light-red silver ore*.

AMMONIURET OF SILVER; BERTHOLLET'S FULMINATING SILVER.—When precipitated oxide of silver is digested in ammonia, a black substance is produced, possessing exceedingly dangerous explosive properties. It explodes while moist when rubbed with a hard body, but when dry, the touch of a feather is sufficient. The ammonia retains some of this substance in solution, and deposits it in small crystals by spontaneous evaporation. A similar compound containing oxide of gold exists. It is easy to understand the reason why these bodies are subject to such violent and sudden decomposition by the slightest cause, on the supposition that they contain an oxide of an easily-reduced metal and ammonia; the attraction between the two constituents of the substance is very feeble, while that between the oxygen of the one and the hydrogen of the other is very powerful. The explosion is caused by the sudden evolution of nitrogen gas and vapor of water, the metal being set free.

A soluble salt of silver is perfectly characterized by the white curdy precipitate of chloride of silver, darkening by exposure to light, and insoluble in hot nitric acid, which is produced by the addition of any soluble chloride. Lead is the only metal which can be confounded with it in this respect, but chloride of lead is soluble to a great extent in boiling water, and is deposited in brilliant acicular crystals when the solution cools. Solutions of silver are reduced to the metallic state by iron, copper, mercury, and other metals.

The economical uses of silver are many; it is admirable for culinary and other similar purposes, not being attacked in the slightest degree by any of the substances used for food. It is necessary, however, in these cases, to diminish the softness of the metal by a small addition of copper. The standard silver of England contains 222 parts of silver and 18 parts of copper.

GOLD.

Gold, in small quantities, is a very widely-diffused metal; traces are constantly found in the iron-pyrites of the more ancient rocks. It is always met with in the metallic state, sometimes beautifully crystallized in the cubic form, associated with quartz, oxide of iron, and other substances in regular mineral veins. The sands of various rivers have long furnished gold derived from this source, and separable by a simple process of washing; such is the *gold-dust* of commerce. When a veinstone is wrought for gold, it is stamped to powder, and shaken in a suitable apparatus with water and mercury; an amalgam is formed, which is afterwards separated from the mixture and decomposed by distillation.

The pure metal is obtained by solution in nitro-hydrochloric acid and precipitation by a salt of protoxide of iron, which, by undergoing peroxidation, reduces the gold. The latter falls as a brown powder, which acquires the metallic lustre by friction.

Gold is a soft metal, having a beautiful yellow color. It surpasses all other metals in malleability, the thinnest gold-leaf not exceeding, it is said, $\frac{1}{200000}$th of an inch in thickness, while the gilding on the silver wire used in the manufacture of *gold-lace*, is still thinner. It may also be drawn into

very fine wire. Gold has a density of 19·5; it melts at a temperature a little above the fusing-point of silver. Neither air nor water affects it in the least at any temperature; the ordinary acids fail to attack it, singly. A mixture of nitric and hydrochloric acids dissolves gold, however, with ease, the active agent being the liberated chlorine. Gold forms two compounds with oxygen, and two corresponding compounds with chlorine, iodine, sulphur, &c. Both oxides refuse to unite with acids.

The equivalent of gold is 99·44. Its symbol is Au (aurum).

Suboxide of gold. Au_2O.—The suboxide is produced when caustic potash in solution is poured upon the subchloride. It is a green powder, partly soluble in the alkaline liquid; the solution rapidly decomposes into metallic gold, which subsides, and into peroxide, which remains dissolved.

Peroxide of gold; auric acid. Au_2O_3.—When magnesia is added to the perchloride of gold, and the sparingly soluble aurate of that base well washed and digested with nitric acid, the peroxide is left as an insoluble reddish-yellow powder, which, when dry, becomes chestnut-brown. It is easily reduced by heat, and also by mere exposure to light; it is slightly soluble in strong acids, but forms with them no definite compounds.

Alkalis dissolve it freely; indeed, the acid properties of this substance are very strongly marked; it partially decomposes a solution of chloride of potassium when boiled with that liquid, potash being produced. When digested with ammonia, it furnishes fulminating gold.

Subchloride of gold. Au_2Cl.—This substance is produced when the perchloride is evaporated to dryness and exposed to a heat of 440°, until chlorine ceases to be exhaled. It forms a yellowish-white mass, insoluble in water. In contact with that liquid, it is decomposed slowly in the cold, and rapidly by the aid of heat, into metallic gold and perchloride.

Perchloride of gold.—Au_2Cl_3.—This is the most important compound of the metal; it is always produced when gold is dissolved in nitro-hydrochloric acid. The deep yellow solution thus obtained, yields, by evaporation, yellow crystals of the double chloride of gold and hydrogen; when this is cautiously heated, hydrochloric acid is expelled, and the residue, on cooling, solidifies to a red crystalline mass of perchloride of gold, very deliquescent, and soluble in water, alcohol, and ether. The perchloride of gold combines with a number of metallic chlorides, forming a series of double salts of which the general formula in the anhydrous state is $MC+Au_2Cl_3$, M representing an equivalent of the second metal. These compounds are mostly yellow when in crystals, and red when deprived of water.

A mixture of chloride of gold with excess of bicarbonate of potash or soda, is used for gilding small ornamental articles of copper; these are cleaned by dilute nitric acid, and then boiled in the mixture for some time, by which means they acquire a thin but perfect coating of reduced gold.

The other compounds of gold are of very little importance.

The presence of this metal in solution may be known by the brown precipitate with protosulphate of iron, fusible before the blow-pipe into a bead of gold; and by the purple compound formed when the chloride of gold is added to a solution of protochloride of tin.

Gold intended for coin, and most other purposes, is always alloyed with a certain proportion of silver or copper, to increase its hardness and durability; the first-named metal confers a pale greenish color. *Gold-leaf* is made by rolling out plates of pure gold as thin as possible, and then beating them be-

tween folds of membrane by a heavy hammer, until the requisite degree of tenuity has been reached. The leaf is made to adhere to wood, &c., by size or varnish.

Gilding on copper has very generally been performed by dipping the articles into a solution of nitrate of mercury, and then shaking them with a small lump of a soft amalgam of gold with that metal, which thus becomes spread over their surfaces; the articles are subsequently heated to expel the mercury, and then burnished. Gilding on steel is done either by applying a solution of perchloride of gold in ether, or by roughening the surface of the metal, heating it, and applying gold-leaf, with a burnisher. Gilding by electrolysis,—an elegant and simple method, now rapidly superseding many of the others,—has already been noticed. The solution usually employed is obtained by dissolving oxide or cyanide of gold in solution of cyanide of potassium.*

MERCURY, OR QUICKSILVER.

This very remarkable metal has been known from an early period, and perhaps more than all others, has excited the attention and curiosity of experimenters, by reason of its peculiar physical properties. Mercury is of great importance in several of the arts, and enters into the composition of many valuable medicaments.

Metallic quicksilver is occasionally met with in globules disseminated through the native sulphuret, which is the ordinary ore. This latter substance, sometimes called *cinnabar*, is found in considerable quantity in several localities, of which the most celebrated are Almaden, in New Castile, and Idria, in Carniola. The metal is obtained by heating the sulphuret in an iron retort with lime or scraps of iron, or by roasting it in a furnace, and conducting the vapors into a large chamber where the mercury is condensed, while the sulphurous acid is allowed to escape. Mercury is imported into this country in bottles of hammered iron containing sixty or seventy pounds each, and in a state of considerable purity. When purchased in smaller quantities, it is sometimes found adulterated with tin and lead, which metals it dissolves to some extent without much loss of fluidity. Such admixture may be known by the foul surface the mercury exhibits when shaken in a bottle containing air, and by the globules, when made to roll upon the table, having a train or tail.

Mercury has a nearly silver-white color, and a very high degree of lustre; it is liquid at all ordinary temperatures, and only solidifies when cooled to —40° F. In this state it is soft and malleable. At 662° it boils, and yields a transparent, colorless vapor, of great density. The metal volatilizes, however, to a sensible extent at all temperatures above 68° or 70°; below this point its volatility is imperceptible. The specific gravity of mercury at 60° is 13·56; that of frozen mercury about 14, great contraction taking place in the act of solidification.

Pure quicksilver is quite unalterable in the air at common temperatures, but when heated to near its boiling-point, it slowly absorbs oxygen, and becomes converted into a crystalline dark-red powder, which is the highest oxide. At a dull red heat, this oxide is again decomposed into its constituents. Hydrochloric acid has little or no action on mercury, and the same may be said of sulphuric acid in a diluted state; when the latter is concentrated, and boiling hot, it oxidizes the metal, converting it into sulphate of the red oxide, with evolution of sulphurous acid. Nitric acid, even dilute and in the cold, dissolves mercury freely.

* Messrs. Elkington, Application of electro-metallurgy to the arts.

Mercury combines with oxygen in two proportions, forming a gray and a red oxide, both of which are salifiable. As the salts of the red oxide are the most stable and permanent, that substance may be regarded as the true protoxide, instead of the gray oxide, to which the term has usually been applied. Until, however, isomorphous relations connecting mercury with the other metals shall be established, the constitution of the two oxides and that of the corresponding chlorides, iodides, &c., must remain somewhat unsettled.

The equivalent of mercury, on the above supposition, will be 101·27; its symbol is Hg (hydrargyrum).

Suboxide of Mercury; Gray Oxide. Hg_2O.—The suboxide is easily prepared by adding caustic potash to the nitrate of this substance, or by digesting calomel in solution of caustic alkali. It is a dark gray heavy powder, insoluble in water. It is slowly decomposed by the action of light into metallic mercury and red oxide. The preparation known in pharmacy by the names *blue pill*, *gray ointment*, *mercury with chalk*, &c., often supposed to owe their efficacy to this substance, merely contain the finely-divided metal.

Protoxide of Mercury; Red Oxide. HgO.—There are three methods by which this compound may be obtained. (1.) By exposing mercury in a glass flask with a long, narrow neck, for several weeks to a temperature approaching 600°; the product has a dark-red color and is highly crystalline; it is the *red precipitate* of the old writers. (2.) By cautiously heating any of the nitrates of either oxide to complete decomposition, when the acid is decomposed and expelled, oxidizing the metal to a maximum, if it happen to be in the condition of suboxide. The product is in this case also crystalline, and very dense, but has a much paler color than the preceding; while hot, it is nearly black. It is by this method that the oxide is generally prepared; it is apt to contain undecomposed nitrate, which may be discovered by strongly heating a portion in a test-tube; if red fumes are produced or the odor of nitrous acid exhaled, the oxide has been insufficiently heated in the process of manufacture. (3.) By adding caustic potash in excess to a solution of corrosive sublimate, by which a bright yellow precipitate of oxide is thrown down, which only differs from the foregoing preparations in being destitute of crystalline texture, and much more minutely divided. It must be well washed, and dried.*

Red oxide of mercury is slightly soluble in water, communicating to the latter an alkaline reaction and metallic taste; it is highly poisonous. When strongly heated, it is decomposed, as before observed, into metallic mercury and oxygen gas.

Nitrates of the Oxides of Mercury.—Nitric acid varies in its action upon mercury, according to the temperature. When cold and somewhat diluted, only salts of the gray oxide are formed, and these are neutral or basic (i. e. with excess of oxide), as the acid or the metal happens to be in excess. When, on the contrary, the nitric acid is concentrated and hot, the mercury is raised to its highest state of oxidation, and a salt of the red oxide produced. Both classes of salts are apt to be decomposed by a large quantity of water, giving rise to insoluble, or sparingly soluble compounds containing an excess of base.

Neutral sub-nitrate, Hg_2O , NO_5+2HO, forms large colorless crystals, soluble in a small quantity of water without decomposition; it is made by dissolving mercury in an excess of cold dilute nitric acid.

When excess of mercury has been employed, a finely-crystallized basic salt is, after some time, deposited, containing $3Hg_2O , 2NO_5+3HO$; this is also decomposed by water. The two salts are easily distinguished when rubbed in a mortar with a little chloride of sodium; the neutral compound gives nitrate

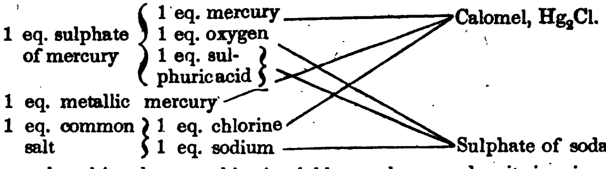
* This precipitate is considered by Schaffner to be a hydrate. HgO , 3HO, for by exposure to the temperature of 392°, it loses water amounting to over 20 per cent. of its weight.—R. B.

of soda and calomel; the basic salt, nitrate of soda and a black compound of calomel with oxide of mercury. A black substance, called *Hahnemann's soluble mercury*, is produced when ammonia in small quantity is dropped into a solution of sub-nitrate; it contains $3Hg_2O$, NO_5+NH_3, or, according to Dr. Kane, $2Hg_2O$. NO_5+NH_3.

Neutral nitrate of the protoxide of mercury, (red oxide,) cannot be obtained in crystals. When hot, strong nitric acid is saturated with red oxide, a crystallized salt separates on cooling, containing $2HgO$, NO_5+2HO; this is also produced by direct solution of the metal. Cold water separates from this substance a yellow insoluble compound which contains $3HgO$, NO_5+HO, and boiling water, a red insoluble salt, $6HgO$, NO_5.—The nitrate of the protoxide of mercury forms several interesting compounds with ammonia.

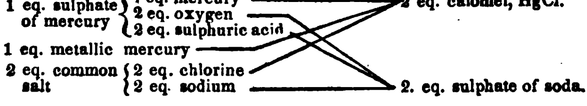
Sulphate of the suboxide of mercury Hg_2O , SO_3, falls as a white crystalline powder when sulphuric acid is added to a solution of the sub-nitrate; it is but slightly soluble in water. *Sulphate of the protoxide*, HgO , SO_3, is readily prepared by boiling together oil of vitriol and metallic mercury until the latter is wholly converted into a heavy white crystalline powder, which is the salt in question; the excess of acid is then removed by evaporation, carried to perfect dryness. Equal weights of acid and metal may be conveniently employed. Water decomposes the sulphate, dissolving out an acid salt and leaving an insoluble, yellow, basic compound, formerly called *turpeth*, or *turbith mineral*, containing, according to Dr. Kane's analysis, $3HgO$, SO_3. Long-continued washing with hot water entirely removes the remaining acid, and leaves pure oxide of mercury.

SUBCHLORIDE OF MERCURY; CALOMEL. Hg_2Cl.—This very important substance may be easily and well prepared by pouring a solution of the sub-nitrate into a large excess of dilute solution of common salt. It falls as a dense white precipitate, quite insoluble in water; it must be thoroughly washed with boiling distilled water, and dried. Calomel is generally procured by another and more complex process. Dry sulphate of the red oxide is rubbed in a mortar with as much metallic mercury as it already contains, and a quantity of common salt, until the globules disappear, and a uniform mixture has been produced. This is subjected to sublimation, the vapor of the calomel being carried into an atmosphere of steam, or into a chamber containing air; it is thus condensed in a minutely-divided state, and the laborious process of pulverization of the sublimed mass avoided. The reaction is thus explained:—*



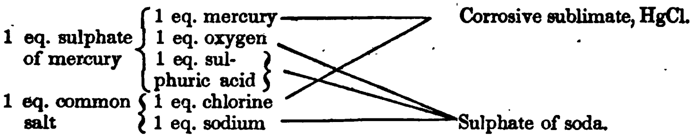
Pure calomel is a heavy, white, insoluble tasteless powder; it rises in vapor at a temperature below redness, and is obtained by ordinary sublimation as a yellowish-white, crystalline mass. It is as insoluble in cold, diluted nitric acid

* If the gray oxide be considered as protoxide, the sulphate will be bisulphate of the peroxide, HgO_2. $2SO_3$, and the decomposition will stand thus:—



as the chloride of silver; boiling-hot, strong nitric acid oxidizes and dissolves it. Calomel is instantly decomposed by an alkali, or by lime-water, with production of suboxide. It is sometimes apt to contain a little chloride, which would be a very dangerous contamination in calomel employed for medical purposes. This is easily discovered by boiling with water, filtering the liquid, and adding caustic potash. Any corrosive sublimate is indicated by a yellow precipitate.*

CHLORIDE OF MERCURY; CORROSIVE SUBLIMATE. $HgCl$.—The chloride may be obtained by several different processes. (1.) When metallic mercury is heated in chlorine gas, it takes fire and burns, producing this substance. (2.) It may be made by dissolving the red oxide in hot hydrochloric acid, when crystals of corrosive sublimate separate on cooling. (3.) Or, more economically, by subliming a mixture of equal parts of sulphate of the protoxide of mercury (red oxide), and dry common salt; and this is the plan generally followed. The decomposition is thus easily explained:—†



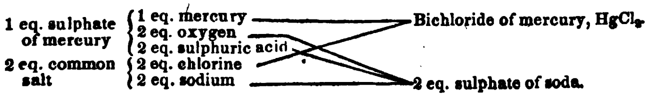
The sublimed chloride forms a white, transparent, crystalline mass of great density; it melts at 509°, and boils and volatilizes at a somewhat higher temperature. It is soluble in 16 parts of cold and 3 of boiling water, and crystallizes from a hot solution in long white prisms. Alcohol and ether also dissolve it with facility; the latter even withdraws it from a watery solution. Chloride of mercury combines with a great number of other metallic chlorides, forming a series of beautiful double salts, of which the ancient *sal alembroth* may be taken as a good example; it contains, $HgCl+NH_4Cl+HO$. Corrosive sublimate absorbs ammoniacal gas with great avidity, generating a compound supposed to contain $2HgCl+NH_3$.

When excess of ammonia is added to a solution of corrosive sublimate, a white, insoluble substance is thrown down, long known under the name of *white precipitate*. Dr. Kane, who has devoted much attention to the salts of mercury, represents this white precipitate as a double amide and chloride of mercury, or $HgCl+HgNH_2$, 2 equivalents of chloride of mercury and one of ammonia, yielding 1 equivalent of the new body and one of hydrochloric acid. A corresponding black compound, $Hg_2Cl+Hg_2NH_2$, is produced when ammonia is digested on calomel, which must be carefully distinguished from the suboxide.

A compound of chloride of mercury with oxide of mercury also exists. It falls as a brown precipitate when a small quantity of ammonia is added to a solution of chloride of mercury, or when carbonate of potash or soda is employed. This substance is also formed by passing chlorine through water holding red oxide of mercury in suspension, or by boiling a mixture of corrosive sublimate and solution of bleaching powder; in the last case it is dark-colored and crys-

* Ammonia is to be preferred, yielding a white precipitate which has less solubility than the red oxide.—R. B.

† Or, on the other supposition—



talline. The oxychloride of mercury contains $HgCl+4HgO$. It is decomposed by heat into corrosive sublimate and red oxide.

Corrosive sublimate forms insoluble compounds with many of the azotized organic principles, as albumen, &c. It is, perhaps, to this property that its great antiseptic virtues are due. Animal and vegetable substances are preserved by it from decay, as in Mr. Kyan's method of preserving timber and cordage. Albumen is on this account an excellent antidote to corrosive sublimate in cases of poisoning.

SUBIODIDE OF MERCURY. Hg_2I.—The subiodide is formed when a solution of iodide of potassium is added to nitrate of the suboxide of mercury; it separates as a dirty-yellow, insoluble precipitate, with a cast of green. It may be prepared by rubbing together in a mortar mercury and iodine in the proportion of 2 equivalents of the former to 1 of the latter, the mixture being moistened from time to time with a little alcohol.

IODIDE OF MERCURY. HgI.—When solution of iodide of potassium is mixed with chloride of mercury, (corrosive sublimate,) a precipitate falls, which is at first yellow, but in a few moments changes to a most brilliant scarlet, which color is retained on drying. This is the neutral iodide; it may be made, although of rather duller tint, by triturating single equivalents of iodine and mercury with a little alcohol. When prepared by precipitation, it is better to weigh out the proper proportions of the two salts, as the iodide is soluble in an excess of either, more especially in excess of iodide of potassium. The iodide of mercury exhibits a very remarkable case of dimorphism, attended with difference of color, the latter being red or yellow according to the figure assumed. Thus, when the iodide is suddenly exposed to a high temperature, it becomes bright yellow throughout, and yields a copious sublimate of minute but brilliant yellow crystals. If in this state it be touched by a hard body, it instantly becomes red, and the same change happens spontaneously after a certain lapse of time. On the other hand, by a very slow and careful heating, a sublimate of red crystals having a totally different form may be obtained, which are permanent. The same kind of change happens with the freshly-precipitated iodide, as Mr. Warington has shown, the yellow crystals first formed breaking up in the course of a few seconds from the passage of the salt to the red modification.*

SUBSULPHURET OF MERCURY. Hg_2S.—The black precipitate thrown down from a solution of subnitrate of mercury by sulphuretted hydrogen, is a subsulphuret; it is decomposed by heat into metallic mercury and neutral sulphuret.

SULPHURET OF MERCURY; ARTIFICIAL CINNABAR; VERMILION. HgS.—Sulphuretted hydrogen gas causes a precipitate of a white color when passed in small quantity into a solution of corrosive sublimate or nitrate of the red oxide; this is a combination of sulphuret with the salt itself. An excess of the gas converts the whole into sulphuret, the color at the same time changing to black. When this black sulphuret is sublimed, it becomes dark-red and crystalline, but undergoes no change of composition; it is then cinnabar. The sulphuret is most easily prepared by subliming an intimate mixture of 6 parts of mercury and 1 of sulphur, and reducing to very fine powder the resulting cinnabar, the beauty of the tint depending much upon the extent to which division is carried. The red or crystalline sulphuret may also be formed directly, without sublimation, by heating the black precipitated substance in a solution of pentasulphuret of potassium; the sulphuret of mercury is in fact soluble to a certain extent in the alkaline sulphurets, and forms with them crystallizable compounds.

* Memoirs of Chemical Society of London, i. p. 86.

When vermilion is heated in the air, it yields metallic mercury and sulphurous acid; it resists the action both of caustic alkali in solution, and of strong mineral acids, even nitric, and is only attacked by aqua regia.

The salts of mercury are all volatilized or decomposed by a temperature of ignition; those which fail to yield the metal by simple heating may in all cases be made to do so by heating in a test-tube with a little dry carbonate of soda. The metal is precipitated from its soluble combinations by a plate of copper, and also by a solution of protochloride of tin, used in excess. The behavior of the chloride and soluble salts of the red oxide with caustic potash and ammonia is also highly characteristic.

Alloys of mercury with other metals are termed *amalgams*; mercury dissolves in this manner many of the metals, as gold, silver, tin, lead, &c. These combinations sometimes take place with considerable violence, as in the case of potassium, where light and heat are produced; besides this, many of the amalgams crystallize after a while, becoming solid. The amalgam of tin used in silvering looking-glasses, and that of silver, sometimes employed for stopping hollow teeth, are examples.

PLATINUM.

Platinum, palladium, rhodium, iridium, and osmium, form a small group of metals, allied in some cases by properties in common, and still more closely by a natural association. *Crude platinum*, a native alloy of platinum, palladium, rhodium, and a little iron, occurs in grains and rolled masses, sometimes of tolerably large dimensions, mixed with gravel and transported materials on the slope of the Ural Mountains in Russia, in Ceylon, and in a few other places. It has never been seen in the rock, which, however, is judged from the accompanying minerals, to have been serpentine.

From this substance platinum is prepared by the following process:—The crude metal is acted upon as far as possible by nitro-hydrochloric acid; to the deep yellowish-red and highly acid solution thus produced, sal-ammoniac is added, by which nearly the whole of the platinum is thrown down in the state of ammonio-chloride. This substance is washed with a little cold water, dried and heated to redness; metallic platinum in spongy state is left. Although this metal cannot be fused in a compact mass by any furnace-heat, yet the same object may be accomplished by taking advantage of its property of welding, like iron, at a very high temperature. The spongy platinum is made into a thin uniform paste with water, introduced into a slightly conical mould of brass, and subjected to a graduated pressure, by which the water is squeezed out, and the mass rendered at length sufficiently solid to bear handling. It is then dried, very carefully heated to whiteness, and hammered, or subjected to powerful pressure by suitable means. If this operation has been properly conducted, the platinum will now be in a state to bear forging into a bar, which can afterwards be rolled into plates, or drawn into wire, at pleasure.

Platinum is in point of color a little whiter than iron; it is exceedingly malleable and ductile, both hot and cold, and is very infusible, melting only before the oxy-hydrogen blow-pipe. It is the heaviest substance known,* its

* This is in accordance with the usual statement, but Iridium (which see) is still denser.—R. B.

specific gravity being 21·5. Neither air, moisture, nor the ordinary acids attack platinum in the slightest degree at any temperature; hence its high value in the construction of chemical vessels. It is dissolved by aqua regia, and superficially oxidized by fused hydrate of potash, which enters into combination with the oxide.

The remarkable property of the spongy metal to determine the union of oxygen and hydrogen has been already noticed. There is a still more curious state in which platinum can be obtained, that of *platinum-black*, where the division is pushed much farther. It is easily prepared by slowly heating to 212°, with frequent agitation, a solution of chloride of platinum to which an excess of carbonate of soda and a quantity of sugar have been added. The black powder is collected on a filter, washed and dried by gentle heat. This substance appears to possess the property of condensing gases, more especially oxygen, into its pores to a very great extent; when placed in contact with a solution of formic acid, it converts the latter, with copious effervescence, into carbonic acid; alcohol and ether dropped upon the platinum-black become changed by oxidation to acetic acid, the rise of temperature being often sufficiently great to cause inflammation. When exposed to a red heat, the black substance shrinks in volume, assumes the appearance of common spongy platinum, and loses these peculiarities, which are no doubt the result of its excessively comminuted state. Platinum forms two compounds with oxygen, chlorine, &c. The equivalent of platinum is 98·68. Its symbol is Pt.

PROTOXIDE OF PLATINUM. PtO.—When protochloride of platinum is digested with caustic potash, a black powder, soluble in excess of alkali, is produced; this is the protoxide. It is soluble in acids with brown color, and the solutions are not precipitated by sal-ammoniac. When peroxide of platinum is heated with solution of oxalic acid, it is reduced to protoxide, which remains dissolved. The liquid has a dark blue color, and deposits fine copper-red needles of oxalate of the protoxide of platinum.

PEROXIDE OF PLATINUM. PtO_2.—This is best prepared by adding nitrate of baryta to sulphate of the peroxide of platinum; sulphate of baryta and nitrate of the oxide are produced. From the latter, caustic soda precipitates one half of the oxide of platinum. The sulphate is itself obtained by acting with strong nitric acid upon the bisulphuret of platinum, which falls as a black powder when a solution of bichloride is dropped into sulphuret of potassium. The hydrate of the peroxide is a bulky brown powder, which, when gently heated, becomes black and anhydrous. It dissolves in acids, and also combines with bases; the salts have a yellow or red tint, and a great disposition to unite with salts of the alkalis and alkaline earths, giving rise to a series of double compounds, which are not precipitated by excess of alkali. A combination of oxide of platinum with ammonia exists, which is explosive. Both oxides of platinum are reduced by ignition.

PROTOCHLORIDE OF PLATINUM. $PtCl$.—The protochloride is produced when bichloride of platinum is exposed for some time to a heat of 400°, by which half of the chlorine is expelled; also, when sulphurous acid is passed into a solution of the bichloride. It is a greenish-gray powder, insoluble in water, but dissolved by hydrochloric acid. The latter solution, mixed with sal-ammoniac or chloride of potassium, deposits a double salt in fine crystals, containing, in the last case, $PtCl+KCl$. The protochloride is decomposed by heat into chlorine and metallic platinum.

PERCHLORIDE OR BICHLORIDE OF PLATINUM. $PtCl_2$.—This substance is always formed when platinum is dissolved in nitro-hydrochloric acid. The acid solution yields on evaporation to dryness a red or brown residue, deliquescent, and very soluble both in water and alcohol; the aqueous solution has a pure orange-yellow tint. Bichloride of platinum combines to form

double salts with a great variety of metallic chlorides; the most important of these compounds are those containing the metals of the alkalis and ammonium. *Chloride of platinum* and *potassium*, $PtCl_2+KCl$, forms a bright-yellow crystalline precipitate, being produced whenever solutions of the chlorides of platinum and of potassium are mixed, or a salt of potash, mixed with a little hydrochloric acid, added to chloride of platinum. It is feebly soluble in water, still less soluble in dilute alcohol, and is decomposed with some difficulty by heat. It is readily reduced by hydrogen at a high temperature, furnishing a mixture of chloride of potassium and platinum-black; the latter substance may thus, indeed, be very easily prepared. The *sodium-salt*, $PtCl_2+NaCl+6HO$, is very soluble, crystallizing in large, transparent, yellow-red prisms, of great beauty. The *ammonio-chloride of platinum*, $PtCl_2+NH_4Cl$, is undistinguishable in physical characters, from the potassium salt; it is thrown down as a precipitate of small, transparent, yellow, octahedral crystals, when sal-ammoniac is mixed with chloride of platinum; it is but feebly soluble in water, still less so in dilute alcohol, and is decomposed by heat, yielding spongy platinum, while sal-ammoniac, hydrochloric acid, and nitrogen, are driven off. Compounds of platinum, with iodine, bromine, sulphur, and phosphorus, have been formed, but are comparatively unimportant.

The bichloride, or a solution of peroxide of platinum, can be at once recognized by the yellow precipitate with sal-ammoniac, decomposable by heat, with production of spongy metal.

Bichloride of platinum and the sodio-chloride of platinum are employed in analytical investigations to detect the presence of potash, and separate it from soda. For the latter purpose, the alkaline salts are converted into chlorides, and in this condition mixed with four times their weight of sodio-chloride of platinum in crystals, the whole being dissolved in a little water. When the formation of the yellow salt appears complete, alcohol is added, and the precipitate collected on a weighed filter, washed with weak spirit, carefully dried, and weighed. The chloride of potassium is then easily reckoned from the weight of the double salt, and this, subtracted from the weight of the mixed chlorides employed, gives that of the chloride of sodium by difference; 100 parts of potassio-chloride of platinum correspond to 35·06 parts of chloride of potassium.

Capsules and crucibles of platinum are of great value to the chemist; the latter are constantly used in mineral analysis for fusing siliceous matter with alkaline carbonates. They suffer no injury in this operation, although the caustic alkali roughens and corrodes the metal. The experimenter must be particularly careful to avoid introducing any oxide of an easily-fusible metal, as that of lead or tin, into a platinum crucible. If reduction should by any means occur, these metals will at once alloy themselves with the platinum, and the vessel will be destroyed. A platinum crucible must never be put naked into the fire, but be always placed within a covered earthen crucible.

PALLADIUM.

The solution of crude platinum, from which the greater part of that metal has been precipitated by sal-ammoniac, is neutralized by carbonate of soda, and mixed with a solution of cyanide of mercury; cyanide of palladium separates as a whitish, insoluble substance, which, on being washed, dried, and

heated to redness, yields metallic palladium in a spongy state. The palladium is then welded into a mass, in the same manner as platinum.

Palladium closely corresponds with platinum in color, appearance, and difficult fusibility; it is also very malleable and ductile. In density it differs very much from that metal, being only 11·8. Palladium is more oxidable than platinum. When heated to redness in the air, especially in the state of sponge, it acquires a blue or purple superficial film of oxide, which is again reduced at a white heat. This metal is slowly attacked by nitric acid; its best solvent is aqua regia. There are two compounds of palladium and oxygen.

The equivalent of palladium is 53·27; its symbol is Pd.

Protoxide of palladium. PdO.—This is obtained by evaporating to dryness, and cautiously heating, the solution of palladium in nitric acid. It is black, and but little soluble in acids. The hydrate falls as a dark brown precipitate, when carbonate of soda is added to the above solution. It is decomposed by a strong heat.

Peroxide of palladium. PdO_2.—The pure peroxide is very difficult to obtain. When solution of caustic potash is poured little by little, with constant stirring, upon the double chloride of palladium and potassium in a dry state, the latter is converted into a yellowish brown substance, which is the peroxide, in combination with water and a little alkali. It is but feebly soluble in acids.

Protochloride of palladium. $PdCl$.—The solution of the metal in aqua regia yields this substance when evaporated to dryness. It is a dark brown mass, soluble in water when the heat has not been too great, and forms double salts, with many metallic chlorides. The potassio and ammonio-chlorides of palladium are much more soluble than those of platinum; they have a dirty-yellow tint.

Perchloride of palladium only exists in solution, and in combination with the alkaline chlorides. It is formed when the protochloride of palladium is digested in aqua regia. The solution has an intense brown color, and is decomposed by evaporation. Mixed with chloride of potassium or sal-ammoniac, it gives rise to a red, crystalline precipitate of double salt, which is but little soluble in water.

A *sulphuret of palladium*, PdS, is formed by fusing the metal with sulphur, or by precipitating a solution of protochloride by sulphuretted hydrogen.

A palladium salt is well marked by the pale yellowish-white precipitate with solution of cyanide of mercury, convertable by heat into the spongy metal.

Palladium is readily alloyed with other metals, as copper; one of these compounds has been applied to useful purposes. A native alloy of gold with palladium is found in the Brazils, and imported into England.

RHODIUM.

The solution from which platinum and palladium have been separated in the manner described, is mixed with hydrochloric acid, and evaporated to dryness. The residue is treated with alcohol of specific gravity ·837, which dissolves everything except the double chloride of rhodium and sodium. This is well washed with spirit, dried, heated to whiteness, and then boiled with water; chloride of sodium is dissolved out, and metallic rhodium remains.

Thus obtained, rhodium is a white, coherent, spongy mass, which is infusible and incapable of being welded. It may be had, however, in a more compact state by fusing it with arsenic or sulphur, and exposing the compound to a high temperature in contact with air. It then acquires a specific gravity of 11.

Rhodium is very brittle; reduced to powder and heated in the air, it becomes oxidized, and the same alteration happens to a greater extent when it is fused with nitrate or bisulphate of potash. None of the acids, singly or conjoined, dissolve this metal, unless it be in the state of alloy, as with platinum, in which case it is attacked by aqua regia.

The equivalent of rhodium is 52·11. Its symbol is R.

Oxide of rhodium. R_2O_3.—Finely-powdered metallic rhodium is heated in a silver crucible with a mixture of hydrate of potash and nitre; the fused mass boiled with water leaves a dark-brown, insoluble substance, consisting of oxide of rhodium in union with potash. This is digested with hydrochloric acid, which removes the potash, and leaves a greenish-gray hydrate of the oxide of rhodium, insoluble in acids. A soluble modification of the same substance, retaining, however, a portion of alkali, may be had by adding an excess of carbonate of potash to the double chloride of rhodium and potassium, and evaporating. Another oxide, containing a smaller proportion of oxygen, is supposed to exist, but has not been obtained in a separate state.

Chloride of rhodium. R_2Cl_3.—The pure chloride is prepared by adding hydrofluosilicic acid to the double chloride of rhodium and potassium, evaporating the filtered solution to dryness, and dissolving the residue in water. It forms a brownish-red deliquescent mass, soluble in water, with a fine red color. It is decomposed by heat into chlorine and metallic rhodium. The *chloride of rhodium and potassium*, $R_2Cl_3+2KCl+2HO$, is prepared by heating in a stream of chlorine a mixture of equal parts finely-powdered rhodium and chloride of potassium. This salt has a fine red color, is soluble in water, and crystallizes in 4-sided prisms. *Chloride of rhodium and sodium* is also a very beautiful red salt, obtained by a similar process; it contains $R_2Cl_3+3NaCl+18HO$. The *chloride of rhodium and ammonium* resembles the potassium compound.

Sulphate of rhodium. $R_2O_3,3SO_3$.—The sulphuret of rhodium, obtained by precipitating one of the salts by a soluble sulphuret, is oxidized by strong nitric acid. The product is a brown powder, nearly insoluble in nitric acid, but dissolved by water; it cannot be made to crystallize. *Sulphate of rhodium and potassium* is produced when metallic rhodium is strongly heated with bisulphate of potash. It is a yellow salt, slowly soluble in cold water.

An alloy of steel with a small quantity of rhodium is said to possess extremely valuable properties.

IRIDIUM.

When crude platinum is dissolved in aqua regia, a small quantity of a black scaly metallic substance usually remains behind, having altogether resisted the action of the acid; this is a native alloy of *iridium*, and *osmium*. It is reduced to powder, mixed with an equal weight of dry chloride of sodium, and heated to redness in a glass tube through which a stream of moist chlorine gas is transmitted. The further extremity of the tube is connected with a receiver containing solution of ammonia. The gas, under these circumstances, is rapidly absorbed, chloride of iridium and chloride of osmium being produced; the former remains in combination with the chloride of sodium; the

latter, being a volatile substance, is carried forward into the receiver, where it is decomposed by the water into osmic and hydrochloric acids, which combine with the alkali. The contents of the tube when cold are treated with water, by which the double chloride of iridium and sodium is dissolved out; this is mixed with an excess of carbonate of soda, and evaporated to dryness. The residue is ignited in a crucible, boiled with water, and dried; it then consists of a mixture of oxide of iron, and a combination of oxide of iridium with soda; it is reduced by hydrogen at a high temperature, and treated successively with water and strong hydrochloric acid, by which the alkali and the iron are removed, while metallic iridium is left in a divided state. By strong pressure and exposure to a white heat, a certain degree of compactness may be communicated to the metal.

Iridium is a white, brittle metal, fusible with great difficulty before the oxy-hydrogen blow-pipe.* It is not attacked by any acid, but is oxidized by fusion with nitre, and by ignition to redness in the air.

The equivalent of iridium is 98·68. Its symbol is Ir.

Oxides of iridium.—Four of these compounds are described. *Protoxide of iridium*, IrO, is prepared by adding caustic alkali to the protochloride, and digesting the precipitate in an acid. It is a heavy black powder, insoluble in acids. It may be had in the state of hydrate by precipitating the protochloride of iridium and sodium by caustic potash. The hydrate is soluble in acids with dirty green color. *Sesquioxide*, Ir_2O_3, is produced when iridium is heated in the air, or with nitre; it is best prepared by fusing in a silver crucible a mixture of carbonate of potash and the perchloride of iridium and potassium, and boiling the product with water. This oxide is bluish-black, and is quite insoluble in acids. It is reduced by combustible substances with explosion. *Binoxide of iridium*, IrO_2, is unknown in a separate state; it is supposed to exist in the sulphate, produced when the sulphuret is oxidized by nitric acid. A solution of sulphate heated with excess of alkali evolves oxygen gas, and deposits sesquioxide of iridium. *Peroxide of iridium*, IrO_3, is produced when carbonate of potash is gently heated with the perchloride of iridium; it forms a grayish-yellow hydrate which contains alkali.

Chlorides of iridium.—*Protochloride*, IrCl, is formed when the metal is brought in contact with chlorine at a dull red heat; it is a dark olive-green, insoluble powder. It is dissolved by hydrochloric acid, and forms double salts with the alkaline chlorides, which have a green color. The *sesquichloride*, Ir_2Cl_3, is prepared by strongly heating iridium with nitre, adding water, and enough nitric acid to saturate the alkali, warming the mixture, and then dissolving the precipitated hydrate of the sesquioxide in hydrochloric acid. It forms a dark yellowish-brown solution. This substance combines with metallic chlorides. *Bichloride* of iridium is obtained in solution by adding hydrofluosilicic acid to the bichloride of iridium and potassium, formed when chlorine is passed over a heated mixture of iridium and chloride of potassium. It forms with metallic chlorides a number of double salts, which resemble the platinum-compounds of the same order. *Perchloride of Iridium*, $IrCl_3$, is unknown in a separate state. *Perchloride of iridium and potassium* is obtained by heating iridium with nitre, and then dissolving the whole in aqua regia, and evaporating to dryness. The excess of chloride of potassium may be extracted by a small quantity of water. The crystallized salt has a beautiful red color. The variety of tints exhibited by the different soluble compounds of iridium is very remarkable, and suggested the name of the metal, from the word iris.

* It is the heaviest substance known, its specific gravity, according to Professor Hare, being 21·8. Proceedings of the Amer. Phil. Soc., May and June, 1842.—R. B.

Platinum, palladium, and iridium, combine with carbon when heated in the flame of a spirit-lamp; they acquire a covering of soot, which when burned leaves a kind of skeleton of spongy metal.

OSMIUM.

The solution of osmic acid in ammonia, already mentioned, is gently heated for some time in a loosely-stopped vessel; its original yellow color becomes darker, and at length a brown precipitate falls, which is a combination of sesquioxide of osmium with ammonia: it results from the reduction of the osmic acid by the hydrogen of the volatile alkali. A little of the precipitate is held in solution by the sal-ammoniac, but may be recovered by heating the clear liquid with caustic potash. The brown substance is dissolved in hydrochloric acid, a little hydrochlorate of ammonia added, and the whole evaporated to dryness. The residue is strongly heated in a small porcelain retort; the oxygen of the oxide combines with hydrogen from the ammonia, vapor of water, hydrochloric acid, and sal-ammoniac, are expelled, and osmium left behind, as a grayish porous mass, having the metallic lustre.

In the most compact state in which this metal can be obtained, it has a bluish-white color, and although somewhat flexible in thin plates, is yet easily reduced to powder. Its specific gravity is 10; it is neither fusible nor volatile. It burns when heated to redness, yielding osmic acid, which volatilizes. Osmiate of potash is produced when the metal is fused with nitre. When in a finely-divided state, it is oxidized by strong nitric acid.

The equivalent of osmium is 99·56. Its symbol is Os.

Oxides of osmium.—Four compounds of osmium with oxygen are known. *Protoxide*, OsO, is obtained, in combination with a little alkali, when caustic potash is added to a solution of protochloride of osmium and potassium. It is a dark green powder, slowly soluble in acids. *Sesquioxide*, Os_2O_3, has already been noticed; it is generated by the de-oxidation of osmiate of ammonia; it is black, and but little soluble in acids. It always contains ammonia, and explodes feebly when heated. *Peroxide of Osmium*, OsO_2, is prepared by strongly heating in a retort a mixture of carbonate of soda and the perchloride of osmium and potassium, and treating the residue with water, and afterwards with hydrochloric acid. The peroxide is a black powder, insoluble in acids, and burning to osmic acid when heated in the air. *Osmic acid*, OsO_4, is by far the most important and interesting of the oxides of this metal. It is prepared by heating osmium in a current of pure oxygen gas; it condenses in the cool part of the tube in which the experiment is made, in colorless transparent crystals. Osmic acid melts and even boils below 212°; its vapor has a peculiar offensive odor, and is exceedingly irritating and dangerous. Water slowly dissolves this substance. It has acid properties, and combines with bases. Nearly all the metals precipitate osmium from a solution of osmic acid.

Chlorides of osmium.—*Protochloride*, $OsCl$, is a dark green crystalline substance formed by gently heating osmium in chlorine gas. It is soluble in a small quantity of water, with green color, but decomposed by a large quantity into osmic and hydrochloric acids, and metallic osmium. It forms double salts with the metallic chlorides. The *sesquichloride*, Os_2Cl_3, has not been isolated; it exists in the solution obtained by dissolving sesquioxide in hydrochloric acid. *Perchloride*, $OsCl_2$, in combination with chloride of potassium, is produced when a mixture of equal parts metallic osmium and the last-named salt is strongly heated in chlorine gas. It forms fine red octahedral crystals, containing $OsCl_2+KCl$.

Osmium combines also with sulphur, and with phosphorus.

PART III.

ORGANIC CHEMISTRY.

INTRODUCTION.

Organic substances, whether directly derived from the vegetable or animal kingdom, or produced by the subsequent modification of bodies which thus originate, are remarkable as a class for a degree of complexity of constitution far exceeding that observed in any of the compounds yet described. And yet the number of elements which enter into the composition of these substances is extremely limited; very few, comparatively speaking, contain more than four, viz., carbon, hydrogen, oxygen, and nitrogen; sulphur and phosphorus are occasionally associated with these in certain natural products, and compounds containing chlorine, iodine, arsenic, &c., have been formed by artificial means. This paucity of elementary bodies is compensated by the very peculiar and extraordinary properties of the four first-mentioned, which possess capabilities of combination to which the remaining elements are strangers. There appears to be absolutely no limit to the number of definite, and often crystallizable, substances which can be thus generated, each marked by a perfect individuality of its own.

The mode of association of the elements of organic substances is in general altogether different from that so obvious in the other division of the science. The latter is invariably characterized by what may be termed a *binary* plan of combination, union taking place between *pairs* of elements, and the compounds so produced again uniting themselves to other compound bodies in the same manner. Thus, copper and oxygen combine to oxide of copper, potassium and oxygen to potash, sulphur and oxygen to sulphuric acid; sulphuric acid, in its turn, combines both with oxide of copper and oxide of potassium, generating a pair of salts, which are again capable of uniting to form the double compound, $CuO, SO_3 + KO, SO_3$.

The most complicated products of inorganic chemistry may be thus shown to be built up by this repeated pairing on the part of their constituents. With organic bodies, however, the case is strikingly different; no such arrangement can here be traced. In sugar, $C_{24}H_{22}O_{22}$, or morphia, $C_{35}H_{20}NO_6$, or the radical of bitter almond oil, $C_{14}H_5O$, and a multitude of similar cases, the elements concerned are, as it were, bound up together into a single whole, which can enter into combination with other substances, and be thence disengaged with properties unaltered.

A curious consequence of this peculiarity is to be found in the comparatively *unstable* character of organic compounds, and their general proneness to decomposition and change, when the balance of opposing forces, to which they owe their existence, becomes deranged by some external cause.

If a complex inorganic substance be attentively considered, it will usually be found that the elements are combined in such a manner as to satisfy the

most powerful affinities, and to give rise to a state of very considerable permanence and durability. But in the case of an organic substance containing three or four elements associated in the way described, this is very far from being true; the carbon and oxygen strongly tend to unite to form carbonic acid; the hydrogen and oxygen attract each other in a powerful manner, and the nitrogen, if that body be present, also contributes its share to these internal sources of weakness by its disposition to generate ammonia. While the opposing forces remain exactly balanced, the integrity of the compound is preserved, but the moment one of them from some accidental cause acquires preponderance over the rest, equilibrium is destroyed, and the organic principle breaks up into two or more new bodies of simpler and more permanent constitution. The agency of heat produces this effect by exalting the attraction of oxygen for hydrogen and carbon; hence the almost universal destructibility of organic substances by a high temperature. Mere molecular disturbance of any kind may cause destruction when the instability is very great.

As a general rule it may be assumed, that those bodies which are most complex from the number of elements, and the want of simplicity in their equivalent relations, are by constitution weakest, and least capable of resisting the action of disturbing forces; and that this susceptibility of change diminishes with increased simplicity of structure, until it reaches its minimum in those bodies which, like the carburets of hydrogen, cyanogen, and oxalic acid, connect, by imperceptible gradations, the organic and the mineral departments of chemical science.

Isomeric bodies, or substances different in properties, yet identical in composition, are of constant occurrence in organic chemistry, and stand, indeed, among its most striking and peculiar features. Every year brings to light fresh examples of compounds so related. In most cases, discordance in properties is fairly and properly ascribed to difference of constitution, the elements being differently arranged. For instance, formic ether, and acetate of methyle, are isomeric, both containing $C_6H_6O_4$; but then the first is by strong analogy, if nothing more, supposed to consist of formic acid, C_2HO_3, combined with ether, C_4H_5O; while the second is imagined, with equal justice, to be made up of acetic acid, $C_4H_3O_3$, and the ether of wood-spirit, C_2H_3O. And this method of explanation is generally sufficient and satisfactory; when it can be shown that a difference of constitution, or even a difference in the equivalent numbers, exists between two or more bodies identical in ultimate composition, the reason of their discordant characters becomes, to a certain extent, intelligible.

Organic bodies may be thus classified:

1. *Quasi elementary substances*, and their compounds. These affect the disposition and characters of the true elements, and, like the latter, evince a tendency to unite on the one hand with hydrogen and the metals, and on the other, with chlorine, iodine, and oxygen. The former are designated *organic salt-radicals*, and the latter, *organic salt basyles*. Comparatively few of either kind have been yet isolated, and it is very possible that very many of them are unable to exist in a separate state. These quasi-elements are at present the most important and interesting substances in organic chemistry.

2. *Organic salt-bases*, not being the oxides of known radicals. The principal members of this class are the vegeto-alkalis; they form crystallizable compounds with acids, organic and inorganic, and even possess in some cases a distinct alkaline reaction to test-paper.

3. *Organic acids*, not being compounds of known radicals. These bodies are very numerous and important. Many of them have an intensely sour

taste, redden vegetable blues, and are almost comparable in chemical energy with the acids of mineral origin.

4. *Neutral non-azotized substances*, containing oxygen and hydrogen in the proportions to form water. The term *neutral* is not strictly correct, as these compounds usually manifest feeble acid properties by combining with metallic oxides. This group comprehends the sugars, the different modifications of starch, gum, &c.

5. *Neutral azotized substances;* the albuminous principles and their allies, the great components of the animal frame. These are in the highest degree complex in constitution, and are destitute of the faculty of crystallization.

6. *Carburets of hydrogen, their oxides and derivatives.*

7. *Fatty bodies.*

8. *Compound acids containing the elements of an organic substance in combination with those of a mineral or other acid.* These bodies form a large and very interesting class, of which sulphovinic acid may be taken as the type or representative.

9. *Coloring principles*, and other substances not referable to either of the preceding classes.

The action of heat on organic substances presents many important and interesting points, of which a few of the more prominent may be noticed. Bodies of simple constitution and of some permanence, which do not sublime unchanged, as many of the organic acids yield, when exposed to a high, but regulated temperature in a retort, new compounds, perfectly definite and often crystallizable, which partake, to a certain extent, of the properties of the original substance; the numerous *pyro-acids*, of which many examples will occur in the succeeding pages, are thus produced. Carbonic acid and water are often eliminated under these circumstances. If the heat be suddenly raised to redness, then the regularity of the decomposition vanishes, while the products become more uncertain and more numerous; carbonic acid and watery vapor are succeeded by inflammable gases, as carbonic oxide and carburetted hydrogen; oily matter and tar distil over, and increase in quantity until the close of the operation, when the retort is found to contain, in most cases, a residue of charcoal. Such is destructive distillation.

If the organic substance contain nitrogen, and be not of a kind capable of taking a new and permanent form at a moderate degree of heat, then that nitrogen is in most instances partly disengaged in the shape of ammonia, partly left in combination with the carbonaceous matter in the distillatory vessel. The products of dry distillation thus become still more complicated.

A much greater degree of regularity is observed in the effects of heat on fixed organic matters when these are previously mixed with an excess of strong alkaline base, as potash or lime. In such cases an acid, the nature of which is chiefly dependent upon the temperature applied, is produced, and remains in union with the base, the residual element or elements escaping in some volatile form. Thus benzoic acid distilled with hydrate of lime, at a dull red heat, yields carbonate of lime and bicarburet of hydrogen, or benzine; woody fibre and caustic potash, heated to a very moderate temperature, yield ulmic acid and free hydrogen; with a higher degree of heat, oxalic acid appears in the place of the ulmic; and at the temperature of ignition, carbonic acid, hydrogen being the other product.

The spontaneous changes denominated *decay* and *putrefaction*, to which many of the more complicated organic, and, more particularly, azotized principles are subject, have lately attracted much attention. By the expression *decay** Liebig and his followers understand a decomposition of moist organic

* Or, *eremacausis*, that is, slow burning.

matter, freely exposed to the air, by the oxygen of which it is gradually burned and destroyed, without sensible elevation of temperature; the term *putrefaction*, on the other hand, is limited to changes occurring in, and beneath the surface of water, the effect being a mere transposition of elements, or metamorphosis of the organic body. The conversion of sugar into alcohol and carbonic acid furnishes, perhaps, the simplest case of the kind. It is proper to remark, however, that contact of oxygen is indispensable, in the first instance, to the change, which, once begun, proceeds without further aid of any other substance, external to the decomposing body, unless it be water or its elements. Every case of putrefaction thus begins with decay; and if the decay or its cause, namely, the absorption of oxygen, be prevented, no putrefaction occurs. The most putrescible substances, as animal flesh intended for food, milk, and highly azotized vegetables, are preserved indefinitely, by enclosure in metallic cases, from which the air has been *completely* removed and excluded.

Some of the curious phenomena of communicated chemical activity, where a decomposing substance seems to involve others in destructive change, which, without such influence, would have remained in a permanent and quiescent state, will be found noticed, in their proper places, as under the head of Vinous fermentation. These actions are yet very obscure, and require to be discussed with great caution.

THE ULTIMATE ANALYSIS OF ORGANIC BODIES.

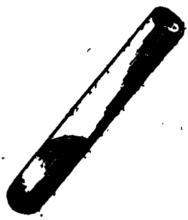
As organic substances cannot be produced at will from their elements, the *analytical* method of research is alone applicable to the investigation of their exact chemical composition; hence the ultimate analysis of these substances becomes a matter of great practical importance. The operation is always executed by causing complete combustion of a known weight of the body to be examined, in such a manner that the carbonic acid and water produced shall be collected, and their quantity determined; the carbon and hydrogen they respectively contain may from these data be easily calculated. When nitrogen, sulphur, phosphorus, chlorine, &c., are present, special and separate means are resorted to for their estimation.

The method to be described for the determination of the carbon and hydrogen owes its convenience and efficiency to the improvements of Professor Liebig: it has superseded all other processes, and is now invariably employed in inquiries of the kind. With proper care, the results obtained are wonderfully correct, and equal, if not surpass in precision, those of the best mineral analyses. The principle upon which the whole depends is the following:—When an organic substance is heated with the oxides of copper, lead, and several other metals, it undergoes complete combustion at the expense of the oxygen of the oxide, the metal being at the same time reduced, either completely, or to a lower state of oxidation. This effect takes place with greatest ease and certainty with the black oxide of copper, which, although unchanged by heat alone, gives up oxygen to combustible matter with extreme facility. When nothing but carbon and hydrogen, or those bodies together with oxygen, are present, one experiment suffices; the carbon and hydrogen are determined directly, and the oxygen by difference.

It is of course indispensable that the substance to be analyzed should possess the physical characters of purity, otherwise the inquiry cannot lead to any good result; if in the solid state, it must also be freed with the most scrupulous care from the moisture, which many substances retain with great obsti-

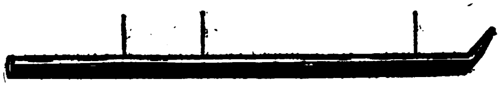
nacy. If it will bear the application of moderate heat, this desiccation is very easily accomplished by a water or steam-bath; in other cases, exposure at common temperatures to the absorbent powers of a large surface of oil of vitriol in the vacuum of an air-pump, must be substituted.

Fig. 143.



The operation of weighing the dried powder is conducted in a narrow open tube about $2\frac{1}{2}$ or 3 inches long; the tube and substance are weighed together, and when the latter has been removed, the tube with any little adherent matter is re-weighed. This weight, subtracted from the former, gives the weight of the substance employed in the experiment. As only 5 or 6 grains are used, the weighings should not involve a greater error than $\frac{1}{100}$th part of a grain. The oxide of copper is best made from the nitrate, by complete ignition in an earthen crucible; it is reduced to powder, and re-heated just before use, to expel hygroscopic moisture, which it absorbs, even while warm, with avidity. The combustion is performed in a tube of hard white Bohemian glass, having a diameter of ·4 or ·5 inch, and in length varying from 10 to 14 inches; this kind of glass bears a moderate red heat without becoming soft enough to lose its shape. One end of the tube is drawn out to a point, as shown in fig. 144, and closed; the other is simply heated to fuse and soften the sharp edges of the glass. The tube is now two-thirds filled with the yet warm oxide of copper, nearly the whole of which is transferred to a small porcelain or Wedgwood mortar, and very intimately mixed with the organic substance. The mixture is next transferred to the tube, and the mortar rinsed with a little fresh and hot oxide, which is added to the rest; the tube is, lastly, filled to within an inch of the open end with oxide from the crucible. A few gentle taps on the table suffice to shake together the contents, so as to leave a free passage for the evolved gases from end to end. The arrangement of the mixture and oxide in the tube is represented in the sketch.

Fig. 144.



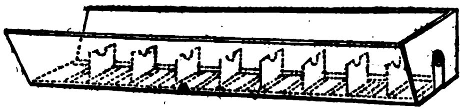
During this mixing operation a little moisture will have been absorbed from the air, however quickly it may have been conducted. To remove this, the tube is connected by a cork to a long tube filled with fragments of chloride of calcium, to which is attached a little exhausting-syringe, screwed to the table. Hot sand, contained in a wooden trough, is placed around the combustion tube, and exhaustion slowly made. After a short interval, the stopcock is opened, and air allowed to enter, which becomes completely dried in its passage inwards. These alternate exhaustions and admissions of dry air are repeated four or five times.

Fig. 145.

Fig. 145 shows the whole arrangement.

The tube is then ready to be placed in the furnace or chauffer; this latter is constructed of thin sheet-iron, and is furnished with a series of supports of equal height, which serve to prevent flexure in the combustion-tube when softened by heat. The chauffer is placed upon flat bricks, or a piece of stone,

Fig. 146.



(*e.* fig. 149,) so that but little air can enter the grating, unless the whole be purposely raised. A slight inclination (*f.* fig. 149) is also given towards the extremity occupied by the mouth of the combustion tube, which passes through a hole provided for the purpose.

To collect the water produced in the experiment, a small light tube of the form represented in fig. 147, filled with fragments of spongy chloride of

Fig. 148.

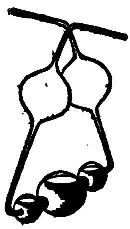
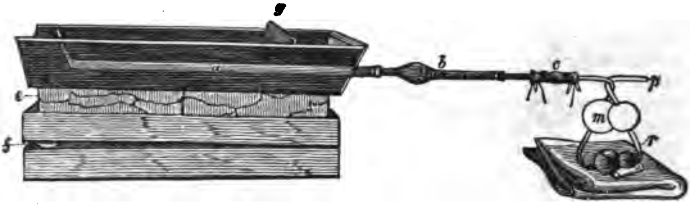


Fig. 147.

calcium, is attached by a perforated cork, thoroughly dried, to the open extremity of the combustion-tube. The carbonic acid is condensed into a solution of caustic potash, of specific gravity 1·25, which is contained in a

small glass apparatus, fig. 148, (*m*. fig. 149,) on the principle of a Woulfe's bottle. The connection between the latter and the chloride of calcium-tube is completed by a little tube of caoutchouc, (*c*. fig. 149,) secured with silk cord. The whole is shown below, as arranged for use. Both the chloride of calcium-tube and the potash-apparatus are weighed with the utmost care before the experiment.

Fig. 149.



Drawing of whole arrangement.

The tightness of the junctions may be ascertained by slightly rarefying the included air by sucking a few bubbles from the interior through the liquid, using the dry lips, or a little bent tube with a perforated cork; if the difference of level of the liquid in the two limbs of the potash-apparatus be preserved for several minutes, the joints are perfect. Red-hot charcoal is now placed around the anterior portion of the combustion-tube, *a*, containing the pure oxide of copper, and when this is red-hot, the fire is slowly extended towards the further extremity by shifting the movable screen *g*, represented in the drawing. The experiment must be so conducted that a uniform stream of carbonic acid shall enter the potash-apparatus by bubbles which may be easily counted; when no nitrogen is present, these bubbles are towards the termination of the experiment almost completely absorbed by the alkaline liquid, the little residue of air alone escaping. In the case of an azotized body, on the contrary, bubbles of gas, nitrogen, pass through the potash-solution during the whole process.

When the tube has become completely heated from end to end, and no more gas is disengaged, but, on the other hand, absorption begins to be evident, the coals are removed from the further extremity of the combustion-tube, and the point of the latter broken off. A little air is drawn through the whole apparatus, by which the remaining carbonic acid and watery vapor are secured. The parts are, lastly, detached, and the chloride of calcium-tube and potash-apparatus re-weighed. The following account of a real experiment will serve as an illustration; the substance examined was crystallized sugar.

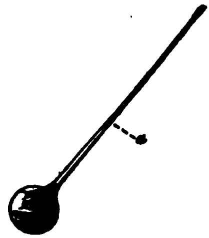
Quantity of sugar employed . . .	4·750 grains.
Potash-apparatus weighed after experiment	781·13
" " before experiment	773·82
Carbonic acid . .	7·31
Chloride of calcium-tube after experiment	226·05
" before experiment	223·30
Water . . .	2·75

7·31 gr. carbonic acid = 1·994 gr. carbon; and 2·75 gr. water = ·3056 gr. hydrogen; or in 100 parts of sugar.*

Carbon	41·98
Hydrogen	6·43
Oxygen, by difference	51·59
	100·

When the organic substance cannot be mixed with the oxide of copper in the manner described, the process must be slightly modified, to meet the particular case. If, for example, a volatile liquid is to be examined, it is enclosed in a little glass bulb with a narrow stem, which is weighed before and after the introduction of the liquid, the point being hermetically sealed. The combustion-tube must have, in this case, a much greater length; and as the oxide of copper cannot be introduced hot, it must be ignited and cooled out of contact with the atmosphere, to prevent absorption of watery vapor. This is most conveniently effected by transferring it, in a heated state, to a large platinum crucible, to which a close-fitting cover may be adapted. When quite cold, the cover is removed, and instantly replaced by a dry glass funnel, by the assistance of which the oxide may be directly poured into the combustion-tube, with mere momentary exposure to the air. A little oxide is put in, then the bulb, with its stem broken at *a*, a file-scratch having been previously made; and, lastly, the tube is filled with the cold and dry oxide of copper. It is arranged in the chauffer, the chloride of calcium-tube and potash-apparatus adjusted, and then, some six or eight inches of oxide having been heated to redness, the liquid in the bulb is, by the approximation of a hot coal, expelled, and slowly converted into vapor, which, in passing over the hot oxide, is completely burned. The experiment is then terminated in the usual manner. Fusible, fatty substances, and volatile concrete bodies, as camphor, require rather different management, which need not be here described.

Fig. 150.



Oxide of copper which has been used may be easily restored by moistening with nitric acid, and ignition to redness; it becomes, in fact, rather improved than otherwise, as after frequent employment its density is increased, and its troublesome hygroscopic powers diminished. For substances which are very difficult of combustion, from the large proportion of carbon they contain, and for compounds into which chlorine enters as a constituent, fused and powdered chromate of lead is very advantageously substituted for the oxide of copper. Chromate of lead freely gives up oxygen to combustible matters, and even evolves, when strongly heated, a little of that gas, which thus ensures the perfect combustion of the organic body.

Analysis of azotized substances.—The presence of nitrogen in an organic compound is easily ascertained by heating a small portion with solid hydrate of potash in a test-tube; the nitrogen, if present, is converted into ammonia, which may be recognized by its odor and alkaline reaction. There are several methods of determining the proportion of nitrogen in azotized organic substances, the experimenter being guided in his choice of means by the nature of the sub-

* The theoretical composition of sugar, $C_{24}H_{22}O_{22}$, reckoned to 100 parts, gives—

Carbon	42·11
Hydrogen	6·43
Oxygen	51·46
	100·

stance and its comparative richness in that element. The carbon and hydrogen are first determined in the usual manner, a longer tube than usual is employed, and four or five inches of its anterior portion filled with spongy metallic copper, made by reducing the oxide by hydrogen; this serves to decompose any nitrous acid or binoxide of nitrogen, which may be formed in the act of combustion. During the experiment, some idea of the abundance or paucity of nitrogen may be formed from the number of bubbles of incondensible gas which traverse the solution of potash.

In the case of compounds abounding in nitrogen, and readily burned by oxide of copper, a method may be employed, which is very easy of execution; this consists in determining the ratio borne by the liberated nitrogen to the carbonic acid produced in the combustion. A tube of hard glass, of the usual diameter, and about 15 inches long, is sealed at one end; a little of the organic substance, mixed with oxide of copper, is introduced and allowed to occupy about two inches of the tube; about as much pure oxide is placed over it, and then another portion of a similar mixture. After which the tube is filled up with a second and larger portion of pure oxide, and a quantity of spongy metallic copper. A short bent tube, made movable by a caoutchouc joint, is fitted by a perforated cork, and made to dip into a mercurial trough, while the combustion-tube itself rests in the chauffer.

Fig. 151.

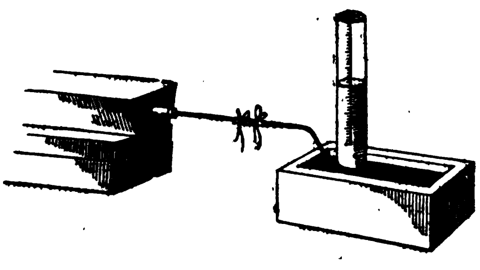


Fig. 152.

Fire is first applied to the anterior part of the tube containing the metal and unmixed oxide, and, when this is red-hot, to the extreme end. Combustion of the first portion of the mixture takes place, the gaseous products sweeping before them nearly the whole of the air of the apparatus. When no more gas issues, the tube is slowly heated by half an inch at a time, in the usual manner, and all the gas very carefully collected in a graduated jar, until the operation is at an end. The volume is then read off, and some strong solution of caustic potash thrown up into the jar by a *pipette* (fig. 152) with a curved extremity. When the absorption is complete, the residual volume of nitrogen is observed, and compared with that of the mixed gases, proper correction being made for differences of level in the mercury, and from these data the exact proportion borne by the nitrogen to the carbon can be at once determined.*

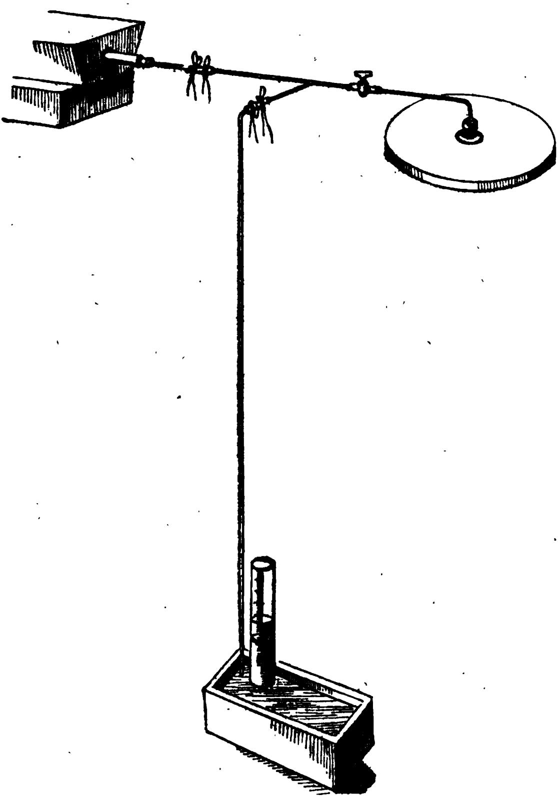
* *Volumes* of the two gases represent *equivalents*, for
100 cubic inches carbonic acid weigh 47·26 grains
100 " nitrogen " 30·14 "
47·26 : 30·14 :: 22 : 14·01

The two last terms are the equivalent numbers: one equivalent of carbonic acid contains besides one equivalent of carbon.

If the proportion of nitrogen be but small, the error from the nitrogen of the residual atmospheric air becomes so great, as to destroy all confidence in the result of the experiment; and the same thing happens when the substance is incompletely burned by oxide of copper; other means must then be employed. The *absolute* method of determination may be had recourse to when the foregoing, or *comparative* method, fails from the first cause mentioned; it gives excellent results, but is very difficult and troublesome in practice, from the accidents to which it is liable.

A tube of good Bohemian glass, 22 inches long, is securely sealed at one end; into this enough carbonate of copper is put to occupy three inches, and upon the copper-salt, a plug of asbestos. A little pure oxide of copper is next

Fig. 153.*



* Fig. 153 represents the principal parts of the arrangement for the absolute estimation of nitrogen. The three-necked tube is shown attached to the plate of the air-pump, and the long tube with recurved lower extremity, terminating beneath a graduated jar standing upon the mercurial trough, and partly filled with strong solution of potash.

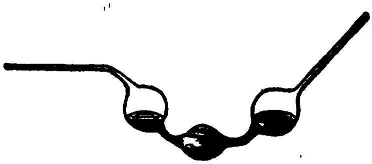
introduced, and afterwards the mixture of oxide and organic substance, the weight of the latter in a dry state having been correctly determined. The remainder of the tube, amounting to nearly one-half of its length, is then filled up with pure oxide of copper, and spongy metal, the two being separated by asbestos, and a round cork, perforated by a piece of narrow tube, is securely adapted to its mouth, and made tight by sealing-wax. The tube is arranged in a trough of hot sand, and put into communication with a powerful and perfect air-pump, by which exhaustion may be made. This is best done by a three-branched tube of brass, furnished with a stop-cock, the third opening being connected with a vertical glass tube, exceeding thirty inches in length, made to dip into a mercurial trough. The joints are formed by caoutchouc connecters, which, when carefully tied, resist without leaking the whole pressure of the atmosphere. Exhaustion is now made as completely as possible; the mercury rises in the long tube, and remains stationary if the numerous joints of the apparatus be perfect. The heat of a spirit-lamp is then applied to the further extremity of the combustion-tube, so as to decompose a portion of the carbonate of copper; the gas depresses the mercurial column, and finally escapes, in considerable quantity, from the delivery-tube. The next step is to remove the sand-trough, and substitute in its place the chauffer, without disturbing the apparatus, now filled with carbonic acid. This done, fire is applied to the tube, commencing at the nearer end, and gradually proceeding to the closed extremity, which yet contains some undecomposed carbonate of copper. This, when the fire at length reaches it, yields up carbonic acid, which chases forward the nitrogen lingering in the tube. During the combustion, the extremity of the delivery-tube is covered by a graduated jar, partly filled with mercury, and partly with strong solution of caustic potash, by which the carbonic acid is wholly absorbed, and nothing left but the nitrogen. When the operation is at an end, the jar, with its contents, is transferred to a vessel of water, and the volume of the nitrogen read off. This is properly corrected for temperature, pressure, and aqueous vapor, and its weight determined by calculation. When the operation has been very successful, and all precautions minutely observed, the result still leaves an error in excess, amounting to ·3 or ·4 per cent., due to the residual air of the apparatus, or that condensed into the pores of the oxide of copper.

A most elegant and admirable process for estimating nitrogen in all organic compounds, except those containing ammonia and nitric acid, has lately been put in practice by MM. Will and Varrentrapp. When a non-azotized organic substance is heated to redness with a large excess of hydrate of potash or soda, it suffers complete and speedy combustion at the expense of the water of the hydrate, the oxygen combining with the carbon of the organic matter to carbonic acid, which is retained by the alkali, while its hydrogen, together with that of the substance, is disengaged, sometimes in union with a little carbon. The same change happens when nitrogen is present, but with this addition: the whole of the nitrogen thus abandoned combines with a portion of the liberated hydrogen to form ammonia. It is evident, therefore, that if this experiment be made on a weighed quantity of matter, and circumstances allow the collection of the whole of the ammonia thus produced, the proportion of nitrogen can be easily calculated.

An intimate mixture is made of 1 part caustic soda, and 2 or 3 parts quicklime, by slaking lime of good quality with the proper proportion of strong caustic soda, drying the mixture in an iron vessel, and then heating it to strong redness in an earthen crucible. The ignited mass is rubbed to powder in a warm mortar, and carefully preserved from the air. The lime is useful in many ways, it diminishes the tendency to deliquescence of the alkali, facilitates mixture with the organic substance, and prevents fusion and liquefac-

tion. A proper quantity of the substance to be analyzed, from five to ten grains, namely, is dried and accurately weighed out; this is mixed in a warm porcelain mortar, with enough of the soda-lime to fill two-thirds of an ordinary combustion-tube, the mortar being rinsed with a little more of the alkaline mixture, and lastly, with a small quantity of powdered glass, which completely removes everything adherent to its surface; the tube is then filled to within an inch of the open end with the lime-mixture, and arranged in the chauffer in the usual manner. The ammonia is collected in a little apparatus of three bulbs containing moderately strong hydrochloric acid, attached by a

Fig. 154.



cork to the combustion-tube. Matters being thus adjusted, fire is applied to the tube, commencing with the anterior extremity. When ignited throughout its whole length, and when no more combustible gas issues from the apparatus, the point of the tube is broken and a little air drawn through the whole. The acid liquid is then emptied into a capsule, the bulbs rinsed into the same with a little alcohol, and then repeatedly with distilled water; an excess of pure chloride of platinum is added, and the whole evaporated to dryness in a water-bath. The dry mass, when cold, is treated with a mixture of alcohol and ether, which dissolves out the superfluous chloride of platinum, but leaves untouched the yellow crystalline double chloride of platinum and ammonium. The latter is collected upon a small weighed filter, washed with the same mixture of alcohol and ether, dried at 212°, and weighed; 100 parts correspond to 6·306 parts of nitrogen; or, the salt with its filter may be very carefully ignited, and the filter burned in a platinum crucible, and the nitrogen reckoned from the weight of the spongy metal, 100 parts of that substance corresponding to 14·25 parts of nitrogen;—the former plan is to be preferred in most cases.

Bodies very rich in nitrogen, as urea, must be mixed with about an equal quantity of pure sugar, to furnish incondensible gas, and thus diminish the violence of the absorption which otherwise occurs; and the same precaution must be taken, for a different reason, with those which contain little or no hydrogen.

Estimation of Sulphur in organic compounds.—When bodies of this class containing sulphur are burned with oxide of copper, a small tube containing peroxide of lead must be interposed between the chloride of calcium-tube and the potash-apparatus to retain any sulphurous acid which may be formed. The proportion of sulphur is determined by oxidizing a known weight of the substance by strong nitric acid, or by fusion with a mixture of nitre and carbonate of potash, and then precipitating the sulphuric acid formed by a barytic salt. Phosphorus is in like manner oxidized to phosphoric acid, the quantity of which is determined by precipitation.

Estimation of Chlorine.—The case of a volatile liquid containing chlorine is of most frequent occurrence, and may be taken as an illustration of the general plan of proceeding. The combustion with oxide of copper, must be very carefully conducted, and two or three inches of the anterior portion of the tube

kept cool enough to prevent volatilization of the chloride of copper into the chloride of calcium-tube. Chromate of lead is much better for the purpose. The chlorine is correctly determined by placing a second small weighed bulb of liquid in a combustion-tube, which is afterwards filled with fragments of pure quick-lime. The lime is brought to a red heat, and the vapor of the liquid driven over it, when the chlorine displaces oxygen from the metal, and gives rise to chloride of calcium. When cold, the contents of the tube are dissolved in the dilute nitric acid and the chlorine precipitated by nitrate of silver.

EMPIRICAL AND RATIONAL FORMULÆ.

A chemical formula is termed *empirical* when it merely gives the simplest possible expression of the composition of the substance to which it refers. A *rational* formula, on the contrary, aims at describing the exact composition of *one equivalent*, or *combining proportion* of the substance, by stating the absolute number of equivalents of each of its elements essential to that object, as well as the mere relations existing between them. The empirical formula is at once deduced from the analysis of the substance, reckoned to 100 parts; the rational requires in addition a knowledge of its combining quantity, which can only be obtained by direct experiment, by synthesis, or by the careful examination of one or more of its most definite compounds. Further, the rational may either coincide with the empirical formula, or it may be a multiple of the latter.

Thus, the composition of acetic acid is expressed by the formula $C_4H_3O_3$, which exhibits the simplest relations of the three elements, and at the same time expresses the quantities of these, in equivalents, required to make up an *equivalent* of acetic acid; hence, it is both empirical and rational. On the other hand, the empirical formula of crystallized kinic acid is $C_7H_6O_6$, while its rational formula, determined by its capacity of saturation, is double, or $C_{14}H_{12}O_{12}$, otherwise written $C_{14}H_{11}O_{11}+HO$.

The deduction of an empirical formula from the ultimate analysis is very easy; the case of sugar, already cited, may be taken as an example. This contains in 100 parts

Carbon	41·98
Hydrogen . . .	6·43
Oxygen	51·59
	100

If each of these quantities be divided by the equivalent of the element, the quotients will express the relation *in equivalents* existing between them; these are afterwards reduced to their simplest expression. This is the only part of the calculation attended with any difficulty; if the numbers were rigidly correct it would only be necessary to divide each by the greatest divisor common to the whole; as they are, however, only approximate, something is of necessity left to the judgment of the experimenter, who is obliged to use more indirect means.

$$\frac{41·98}{6} = 6·99;\ 6·43;\ \frac{51·59}{8} = 6·44,$$

or 699 eq. carbon, 643 eq. hydrogen, and 644 eq. oxygen.

It will be evident, in the first place, that the hydrogen and oxygen are present in the proportions to form water, or as many equivalents of one as of the other. Again, the equivalents of carbon and hydrogen are nearly in the pro-

portion of 12 : 11, so that the formula $C_{12}H_{11}O_{11}$ appears likely to be correct. It is now easy to see how far this is admissible by reckoning it back to 100 parts, comparing the result with the numbers given by the actual analysis, and observing whether the difference falls fairly in direction and amount within the limits of error of what may be termed a good experiment, viz., two or three-tenths per cent. *deficiency* in the carbon, and not more than one-tenth per cent. *excess* in the hydrogen.

Carbon	$6\times12=72$
Hydrogen	11 eq.=11
Oxygen	$8\times11=88$
	171

$$171 : 72 :: 100 : 42{\cdot}11$$
$$171 : 11 :: 100 : 6{\cdot}43$$
$$171 : 88 :: 100 : 51{\cdot}46$$

Organic acids and salt-radicals have their proper equivalents most frequently determined by an analysis of their lead and silver-salts, by burning these latter with suitable precautions in a thin porcelain capsule, and noting the weight of the oxide of led, or metallic silver left behind. If the oxide of lead be mixed with globules of reduced metal, the quantity of the latter must be ascertained by dissolving away the oxide by acetic acid. Or, the lead-salt may be converted into sulphate, and the silver-compound into chloride, and both metals thus estimated. An organic base, on the contrary, or a basyle, has its equivalent fixed by the observation of the quantity of a mineral acid, or an inorganic salt-radical, required to form with it a combination having the characters of neutrality.

DETERMINATION OF THE DENSITY OF VAPORS.

The determination of the specific gravity of the vapor of a volatile substance is frequently a point of great importance, inasmuch as it gives the means, in conjunction with the analysis, of representing the constitution of the substance by measure in a gaseous state. The following is a sketch of the plan of operation usually followed:—A light glass globe about three inches in diameter is taken, and its neck softened and drawn out in the blow-pipe flame, as represented in the figure in the margin; this is accurately weighed. About one hundred grains of the volatile liquid are then introduced, by gently warming the globe and dipping the point into the liquid, which is then forced upwards by the pressure of the air as the vessel cools. The globe is next firmly attached by wire to a handle in such a manner that it may be plunged into a bath of boiling water or heated oil, and steadily held with the point projecting upwards. The bath must have a temperature considerably above that of the boiling-point of the liquid. The latter becomes rapidly converted into vapor, which escapes by the narrow orifice, chasing before it the air of the globe. When the issue of vapor has wholly ceased, and the temperature of the bath, carefully observed, appears pretty uniform, the open extremity of the point is hermetically sealed by a small blow-pipe flame. The globe is removed from the bath, suffered to cool, cleansed if necessary, and weighed, after which the neck is broken off beneath the surface of water or mercury. The liquid enters the globe, and if the

Fig. 155.

expulsion of the air by the vapor has been complete, fills it; if otherwise, an air-bubble is left, whose volume can be easily ascertained by pouring the liquid from the globe into a jar graduated to cubic inches, and then re-filling the globe, and repeating the same observation. The capacity of the vessel is thus at the same time known; and these are all the data required. An example will render the whole intelligible.

Determination of the density of the vapor of Acetone.

Capacity of globe	31·61 cubic inches.
Weight of globe filled with dry air at 52° F., and 30·24 inches barometer	2070·88 grains.
Weight of globe filled with vapor at 212°, (temp. of the bath at the moment of sealing the point,) and 30·24 inches barometer	2076·81 grains.
Residual air, at 45° F., and 30·24 in bar. . .	·60 cubic inch.

31·61 cub. inches of air at 52° and 30·24 in. bar. = 32·36 cub. inches at 60° and 30 inch. bar., weighing . . . 10·035 grains.
Hence, weight of empty globe, 2070·88—10·035 = 2060·845 grains.

6 c. inch. of air at 45° = ·8 c. inch at 212°; weight of do. by calculation = ·191 grain.
31·61 —·8 = 30·81 cubic inches of vapor at 212° and 30·24 in. bar. which, *on the supposition that it could bear cooling to* 60° *without liquefaction*, would at that temperature, and under a pressure of 30 inch. bar., become reduced to 24·18 cubic inches.

Hence,

Weight of globe and vapor	2076·810 grains.
" residual air	·191
	2076·619
Weight of globe	2060·845
Weight of the 24·18 cubic inches of vapor . .	15·774
Consequently 100 cubic inches of such vapor must weigh	65·23 grains.
100 cubic inches of air, under similar circumstances, weigh	31·01

$\frac{65{\cdot}23}{31{\cdot}01} = 2{\cdot}103$, the specific gravity of the vapor in question, air being unity.

In the foregoing statement a correction has been, for the sake of simplicity, omitted, which in very exact experiments must not be lost sight of, viz., the expansion and change of capacity of the glass globe by the elevated temperature of the bath. The density so obtained will be always on this account a little too high.

The error to which the mercurial thermometer is, at high temperatures, liable, tends in the opposite direction.

SECTION I.

NON-AZOTIZED BODIES.

SACCHARINE AND AMYLACEOUS SUBSTANCES, AND THE PRODUCTS OF THEIR ALTERATIONS.

The members of this remarkable and very natural group present several interesting cases of isomerism. They are characterized by their feeble aptitude to enter into combination, and also by containing, with perhaps one exception, oxygen and hydrogen in the proportions to form water.

Table of Saccharine and Amylaceous substances.

Cane-sugar, crystallized	$C_{24}H_{22}O_{22}$
Cane-sugar, in combination	$C_{24}H_{18}O_{18}$
Grape-sugar, crystallized	$C_{24}H_{28}O_{28}$
Grape-sugar, in combination	$C_{24}H_{21}O_{21}$
Milk-sugar, crystallized	$C_{24}H_{24}O_{24}$
Milk-sugar, in combination	$C_{24}H_{19}O_{19}$
Sugar of *eucalyptus*, crystallized	$C_{24}H_{28}O_{28}$
Sugar from *secale cornutum*	$C_{24}H_{26}O_{26}$
Mannite	$C_6H_7O_6$
Starch, unaltered, dried at 212°	$C_{24}H_{20}O_{20}$
Amidine, or gelatinous starch	$C_{24}H_{20}O_{20}$
Dextrine, or gummy starch	$C_{24}H_{20}O_{20}$
Starch from *cetraria Islandica*	$C_{24}H_{20}O_{20}$
Inuline	$C_{24}H_{21}O_{21}$
Gum-arabic	$C_{24}H_{22}O_{22}$
Gum-tragacanth	$C_{24}H_{20}O_{20}$
Lignine, or cellulose	$C_{24}H_{20}O_{20}$

CANE-SUGAR; ORDINARY SUGAR. $C_{24}H_{22}O_{22}$.—This most useful substance is found in the juice of many of the grasses, in the sap of several forest-trees, in the root of the beet and the mallow, and in several other plants. It is extracted most easily and in greatest abundance from the sugar-cane, cultivated for the purpose in many tropical countries. The canes are crushed between rollers, and the expressed juice mixed with a small quantity of hydrate of lime, and rapidly heated to near the boiling-point. The clear liquid separated from the coagulum thus produced, is rapidly evaporated in an open pan, and when the due degree of concentration has been reached, transferred to a shallow vessel, and left to crystallize, during which time it is frequently agitated in order to hasten the change and hinder the formation of large crystals. It is, lastly, drained from the dark uncrystallizable syrup, or *molasses*, and sent into commerce under the name of *raw* or *Muscovado* sugar. The refining of this crude product is effected by redissolving it in water, adding a quantity of albumen in the shape of serum of blood or white of egg, and sometimes a little lime-water, and heating the whole to the boiling-point; the albumen coagu-

lates, and forms a kind of net-work of fibres, which enclose and separate from the liquid all mechanically suspended impurities. The solution is decolorized by filtration through animal charcoal, evaporated to the crystallizing-point, and put into conical earthen moulds, where it solidifies, after some time, to a confusedly-crystalline mass, which is drained, washed with a little clean syrup, and dried in a stove; the product is ordinary loaf sugar. When the crystallization is allowed to take place quietly and slowly, *sugar-candy* results, the crystals under these circumstances acquiring large volume and regular form. The evaporation of the decolorized syrup is best conducted in strong close boilers exhausted of air; the boiling-point of the syrup is reduced in consequence from 230° to 150° or below, and the injurious action of the heat upon the sugar in great measure prevented. Indeed the production of molasses in the rude Indian manufacture is entirely the result of the high and long-continued heat applied to the cane-juice, and might be almost entirely prevented by the use of vacuum-pans, the product of sugar being thereby greatly increased in quantity, and so far improved in quality as to become almost equal to the refined article.

In many parts of the continent of Europe sugar is manufactured on a large scale from beet-root, which contains about 8 per cent. of that substance. The process is far more complicated and troublesome than that just described, and the product much inferior. When refined, however, it is scarcely to be distinguished from the preceding. The inhabitants of the Western states of America prepare sugar in considerable quantity from the sap of the sugar-maple, *acer saccharinum*, which is common in those parts. The tree is tapped in the spring by boring a hole a little way into the wood, and inserting a small spout to convey the liquid into a vessel placed for its reception. This is boiled down in an iron pot, and furnishes a coarse sugar, which is almost wholly employed for domestic purposes, but little finding its way into commerce.

Pure sugar slowly separates from a strong solution in large, transparent colorless crystals, having the figure of a modified oblique rhombic prism. It has a pure, sweet taste, is very soluble in water, requiring for solution only one-third of its weight in the cold, and is also dissolved by alcohol, but with more difficulty. When moderately heated it melts, and solidifies on cooling, to a glassy amorphous mass, familiar under the name of *barley* sugar; at a higher temperature, it blackens, and suffers decomposition, and the same effect is produced, as already remarked, by long-continued boiling on the aqueous solution, which loses its faculty of crystallizing, and acquires color. The crystals have a specific gravity of 1·6, and are unchanged in the air.

The deep brown soluble substance called *caramel*, used for coloring spirits, and other purposes, is a product of the action of heat upon cane-sugar. It contains $C_{24}H_{18}O_{18}$, and is isomeric with cane-sugar in combination.

The following is the composition assigned to the principal compounds of cane-sugar by M. Péligot, who has devoted much attention to the subject.*

Crystallized cane-sugar . . .	$C_{24}H_{18}O_{18}+4HO$
Compound of sugar with common salt	$C_{24}H_{18}O_{18}+NaCl+3HO$
Compound of sugar with baryta .	$C_{24}H_{18}O_{18}+2BaO+4HO$
Compound of sugar with lime .	$C_{24}H_{18}O_{18}+2CaO+4HO$
Compound of sugar with oxide of lead	$C_{24}H_{18}O_{18}+4PbO$

The compounds with baryta and lime are prepared by digesting sugar at a gentle heat with the hydrates of the earths. The lime compound has a bitter taste, and is more soluble in cold water than in hot. Both are readily decom-

* Ann. Chim. et Phys., lxvii. p. 113.

posed by carbonic acid, crystals of carbonate of lime being occasionally produced. The combination with oxide of lead is prepared by mixing sugar with solution of acetate of lead, adding excess of ammonia, and drying the white insoluble product out of contact with air. The compound with common salt is crystallizable, soluble, and deliquescent.

GRAPE SUGAR; GLUCOSE; SUGAR OF FRUITS. $C_{24}H_{28}O_{28}$.—This variety of sugar is very abundantly diffused through the vegetable kingdom; it may be extracted in large quantity from the juice of sweet grapes, and also from honey, of which it forms the solid crystalline portion, by washing with cold alcohol, which dissolves the fluid syrup. It may also be prepared by artificially modifying cane-sugar, starch, and woody fibre, by processes presently to be described. The appearance of this substance, to an enormous extent in the urine, is the most characteristic feature of the fatal disease called *diabetes*.

Grape-sugar is easily distinguished by several important peculiarities from cane-sugar; it is much less sweet, and less soluble in water, requiring 1½ parts of the cold liquid for solution. Its mode of crystallization is also completely different; instead of forming, like cane-sugar, bold, distinct crystals, it separates from its solutions in water and alcohol in granular warty masses, which but seldom present crystalline faces. When pure, it is nearly white. When heated it melts, and loses 4 eq. of water, and at a higher temperature blackens, and suffers decomposition. Grape-sugar combines with difficulty with lime, baryta, and oxide of lead, and is converted into a brown or black substance when boiled with solution of caustic alkali, by which cane-sugar is but little affected. It dissolves, on the contrary, in strong oil of vitriol without blackening, and gives rise to a peculiar compound acid, whose baryta-salt is soluble. Cane-sugar is, under these circumstances, instantly changed to a black mass resembling charcoal.

When solutions of cane and grape-sugar are mixed with two separate portions of solution of sulphate of copper, and caustic potash added in excess to each, deep blue liquids are obtained, which, on being heated, exhibit different characters; the one containing cane-sugar is at first but little altered; a small quantity of red powder falls after a time, but the liquid long retains its blue tint; with the grape-sugar, on the other hand, the first application of heat throws down a copious greenish precipitate which rapidly changes to scarlet, and eventually to dark red, leaving a nearly colorless solution. This is an excellent test for distinguishing the two varieties of sugar, or discovering an admixture of grape with cane-sugar.

Grape-sugar unites with common salt, forming a soluble compound of sweetish saline taste, which crystallizes in a regular and beautiful manner.

Compounds of Grape-sugar, according to Péligot.

Crystalline grape-sugar, dried in the air .	$C_{24}H_{21}O_{21}+7HO$
The same, dried at 266°	$C_{24}H_{21}O_{21}+3HO$
Compound of grape-sugar with common salt	$C_{24}H_{21}O_{21}+NaCl+5HO$
The same, dried at 266°	$C_{24}H_{21}O_{21}+NaCl+2HO$
Compound of grape-sugar with baryta .	$C_{24}H_{21}O_{21}+3BaO+7HO$
Compound of grape-sugar with lime .	$C_{24}H_{21}O_{21}+3CaO+7HO$
Compound of grape-sugar with oxide of lead	$C_{24}H_{21}O_{21}+6PbO$

Sulphosaccharic acid. $C_{24}H_{20}O_{20},SO_3$.—Melted grape-sugar is cautiously mixed with concentrated sulphuric acid, the product dissolved in water, and neutralized with carbonate of baryta; sulphate of baryta is formed together with a soluble sulphosaccharate of that earth, from which the acid itself may

be afterwards eliminated. It is a sweetish liquid, forming a variety of soluble salts, and very prone to decompose into sugar and sulphuric acid.

Action of dilute acids upon sugar.—Cane-sugar dissolved in dilute sulphuric acid is gradually but completely converted, at the common temperature of the air, into grape sugar. The same solution, when long boiled, yields a brownish-black and nearly insoluble substance, which is a mixture of two distinct bodies, one having the appearance of small shining scales, and the other that of a dull brown powder. The first, called by Boullay and Malaguti *ulmine*, and by Liebig *sachulmine*, is insoluble in ammonia and alkalis; the second, *ulmic acid*, the *sachulmic acid* of Liebig, dissolves freely, yielding dark brown solutions precipitable by acids. By long-continued boiling with water, sachulmic acid is converted into sachulmine. Both these substances have the same composition, expressed by the empirical formula C_2HO. Hydrochloric acid, in a dilute state, produces the same effects.*

Action of alkalis upon sugar.—When lime or baryta is dissolved in a solution of grape sugar, and the whole left to itself several weeks in a close vessel, the alkaline reaction will be found to have disappeared from the formation of an acid substance. By mixing this solution with subacetate of lead, a voluminous white precipitate is obtained, which, when decomposed by sulphuretted hydrogen, yields sulphuret of lead, and the new acid, to which the term *kalisaccharic*, or *glucic*, is applied. Glucic acid is very soluble and deliquescent, has a sour taste, and acid reaction; its salts, with the exception of that containing oxide of lead, are very soluble. It contains $C_8H_5O_5$. When grape-sugar is heated in a strong solution of potash, soda, or baryta, the liquid darkens, and at length assumes a nearly black color. The addition of an acid then gives rise to a black flocculent precipitate of a substance called *melasinic* acid, containing $C_{24}H_{12}O_{10}$. Cane-sugar long boiled with alkalis undergoes the same changes, being probably first converted into grape-sugar.

SUGAR OF THE EUCALYPTUS, described by Professor Johnson,† closely resembles ordinary grape-sugar in many particulars, and has the same composition.

SUGAR FROM ERGOT OF RYE.—This variety of sugar, extracted by alcohol from the ergot, crystallizes in transparent colorless prisms, which have a sweet taste, and are very soluble in water. It differs from cane-sugar in not reducing the acetate of copper when boiled with a solution of that substance. It contains $C_{24}H_{62}O_{26}$.

SUGAR OF DIABETES INSIPIDUS.—A substance having the other properties of a sugar, but destitute of sweet taste, has been described by M. Thenard as having been obtained from the above-mentioned source. It was capable of furnishing alcohol by fermentation, and of suffering conversion into grape-sugar by dilute sulphuric acid. Its composition is unknown.

LIQUORICE-SUGAR; GLYCYRRHIZINE.—The root of the common liquorice yields a large quantity of a peculiar sweet substance which is very soluble in water, but refuses to crystallize; it is remarkable for forming with acids com-

* Under the names *ulmine* and *ulmic acid* have been confounded a number of brown or black, uncrystallizable substances, produced by the action of powerful chemical agents upon sugar, lignine, &c., or generated by the putrefactive decay of vegetable fibre. Common garden mould, for example, treated with dilute, boiling solution of caustic potash, yields a deep brown solution, from which acids precipitate a flocculent, brown substance, having but a slight degree of solubility in water. This is generally called *ulmic* or *humic* acid, and its origin ascribed to the reaction of the alkali on the *ulmine* or *humus* of the soil. It is known that these bodies differ exceedingly in composition; they are too indefinite to admit of ready investigation.

† Memoirs of Chemical Society of London, i. 159.

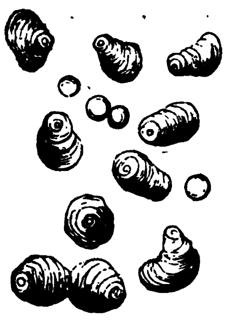
pounds which have but sparing solubility. Glycyrrhizine cannot be made to ferment.

SUGAR OF MILK; LACTINE. $C_{24}H_{24}O_{24}$.—This curious substance is an important constituent of milk; it is obtained in large quantities by evaporating *whey* to a syrupy state, and purifying the lactine, which slowly crystallizes out by animal charcoal. It forms white, translucent four-sided prisms of great hardness. It is slow and difficult of solution in cold water, requiring for that purpose 5 or 6 times its weight; it has a feeble sweet taste, and in the solid state feels gritty between the teeth. When heated, it loses water, and at a high temperature blackens and decomposes. Milk-sugar forms several compounds with oxide of lead, and is converted into grape-sugar by boiling with dilute mineral acids. It is not directly fermentable, but can be made under particular circumstances to furnish alcohol.

MANNA-SUGAR; MANNITE. $C_6H_7O_6$.—This is the chief component of *manna*, an exudation from a species of ash; it is also found in the juice of certain other plants, and in several sea-weeds; and may be formed artificially from ordinary sugar by a peculiar kind of fermentation. It is best prepared by treating manna with boiling alcohol, and filtering the solution whilst hot; the mannite crystallizes on cooling in tufts of slender colorless needles. It is fusible by heat without loss of weight, is freely soluble in water, possesses a powerfully sweet taste, and has no purgative properties. Mannite refuses to ferment. The substance formerly described as *mushroom-sugar* is merely mannite.

STARCH; FECULA.—This is one of the most important and widely-diffused of the vegetable proximate principles, being found to a greater or less extent in every plant. It is most abundant in certain roots and tubers, and in soft stems; seeds often contain it in large quantity. From these sources the fecula can be obtained by rasping or grinding to pulp the vegetable structure, and washing the mass upon a sieve, by which the torn cellular tissue is retained, while the starch passes through with the liquid, and eventually settles down from the latter as a soft, white, insoluble powder, which may be washed with cold water, and dried with very gentle heat. Potatoes treated in this manner yield a large proportion of starch. Starch from grain may be prepared in the same manner by mixing the meal with water to a paste, and washing the mass upon a sieve; a nearly white, insoluble substance called *gluten* remains behind, which contains a large proportion of nitrogen. The gluten of wheat flour is extremely tenacious and elastic. The value of meal as an article of food greatly depends upon this substance. Starch from grain is commonly manufactured on the large scale by steeping the material in water for a considerable period, when the lactic acid, always developed under such circumstances from the sugar of the seed, disintegrates, and in part dissolves the azotized matter, and greatly facilitates the mechanical separation of that which remains. A still more easy and successful process has lately been introduced, in which a very dilute solution of caustic soda, containing about 200 grains of alkali to a gallon of liquid, is employed with the same view. Excellent starch is thus prepared from rice. Starch is insoluble in cold water, as indeed its mode of preparation sufficiently shows; it is equally insoluble in alcohol and other liquids, which do not effect its decomposition. To the naked eye it presents the appearance of a soft, white, and often glistening powder; under the microscope it is seen to be altogether destitute of crystalline, but to possess, on the contrary, a kind of organization, being made up of multitudes of little rounded transparent bodies, upon each of which a series of depressed parallel rings surrounding a central spot or hilum, may often be traced. The starch-granules from different plants vary both in magnitude and form; those from the *canna coccinea*, or *tous les mois*, and potato being largest; and those from wheat and

Fig. 156.



the cereals in general, very much smaller. The figure in the margin will serve to convey an idea of the appearance of the granules of potato-starch highly magnified.

When a mixture of starch and water is heated to near the boiling-point of the latter, the granules burst and disappear, producing, if the proportion of starch be considerable, a thick gelatinous mass, very slightly opalescent from the shreds of fine membrane, the envelop of each separate granule. By the addition of a large quantity of water, this gelatinous starch, or *amidine*, may be so far diluted, as to pass in great measure through filter-paper. It is very doubtful, however, how far the substance itself is really soluble in water, at least when cold; it is more likely to be merely suspended in the liquid in the form of a swollen, transparent, insoluble jelly, of extreme tenuity. Gelatinous starch, exposed in a thin layer to a dry atmosphere, becomes converted into a yellowish, horny substance, like gum, which, when put into water, again softens and swells.

Thin gelatinous starch is precipitated by many of the metallic oxides, as lime, baryta, and oxide of lead, and also by a large addition of alcohol. Infusion of galls throws down a copious yellowish precipitate containing tannic acid, which re-dissolves when the solution is heated. By far the most characteristic reaction, however, is that with free iodine, which forms with starch a deep indigo-blue compound, which appears to dissolve in pure water, although it is insoluble in solutions containing free acid or saline matter. The blue liquid has its colors destroyed by heat, temporarily, if the heat be quickly withdrawn, and permanently, if the boiling be long continued, in which case the compound is decomposed, and the iodine volatilized. Starch in the dry state, put into iodine-water, acquires a purplish-black color.

The unaltered and the gelatinous starch, in a dried state, have the same composition, namely, $C_{24}H_{20}O_{20}$; a compound of starch and oxide of lead was found to contain, when dried at 212°, $C_{24}H_{18}O_{18}+4PbO$.*

DEXTRINE.—When gelatinous starch is boiled with a small quantity of dilute sulphuric, hydrochloric, or indeed almost any acid, it speedily loses its consistency, and becomes thin and limpid from having suffered conversion into a soluble substance resembling gum, called dextrine.† The experiment is most conveniently made with sulphuric acid, which may be afterwards withdrawn by saturation with chalk. The liquid, filtered from the nearly insoluble gypsum, may then be evaporated in a water-bath to dryness. The result is a gum-like mass, destitute of crystalline structure, soluble in cold water, and precipitable from its solution by alcohol, and capable of combining with oxide of lead. Iodine sometimes produces in a solution of dextrine a purplish-red tint, and sometimes occasions no change.

When the ebullition with the dilute acid is continued for a considerable period, the dextrine first formed undergoes a further change, and becomes converted into grape-sugar, which can be thus artificially produced with the greatest facility. The length of time required for this remarkable change depends upon the quantity of acid present; if the latter be very small, it is necessary to continue the boiling many successive hours, replacing the water which evaporates. With a larger proportion of acid, the conversion is much

* Payen, Ann. de Ch. et Ph. t. 65, 249.

† From its action on polarized light, twisting the plane of polarization *towards the right hand*.

more speedy. A mixture of 15 parts potato-starch, 60 parts water, and 6 parts sulphuric acid, may be kept boiling for about four hours; the liquid neutralized with chalk, filtered, and rapidly evaporated to a small bulk. By digestion with animal charcoal, and a second filtration, much of the color will be removed, after which the solution may be boiled down to a thin syrup and left to crystallize; in the course of a few days it solidifies to a mass of grape-sugar. There is another method of preparing this substance from starch which deserves particular notice. Germinating seeds, and buds in the act of development, are found to contain a small quantity of a peculiar azotized substance, formed at this particular period from the gluten or vegetable albuminous matter, to which the name *diastase* is given. The substance possesses the same curious property of effecting the conversion of starch into dextrine, and ultimately into grape-sugar, and at a much lower temperature than that of ebullition. A little infusion of malt, or germinated barley, in tepid water, mixed with a large quantity of thick gelatinous starch, and the whole maintained at 160° or thereabouts, occasions complete liquefaction in the space of a few minutes from the production of dextrine, which in its turn becomes in three or four hours converted into sugar. If a greater degree of heat be employed, the diastase is coagulated and rendered insoluble and inactive. Very little is known respecting diastase itself; it seems very much to resemble vegetable albumen, but has never been got in a state of purity.

The change of starch or dextrine into sugar, whether produced by the action of dilute acid or by diastase, takes place quite independently of the oxygen of the air, and is unaccompanied by any secondary product. The acid takes no direct part in the reaction; it may, if not volatile, be all withdrawn without loss after the experiment. The whole affair lies between the starch and the elements of water; a fixation of the latter occurring in the new product, as will be seen at once on comparing their composition. The sugar, in fact, so produced very sensibly exceeds in weight the starch employed. Dextrine itself has exactly the same composition as the original starch.

Dextrine is used in the arts as a substitute for gum; it is sometimes made in the manner above described, but more frequently by heating dry potato-starch to 400°, by which it acquires a yellowish tint and becomes soluble in cold water. It is sold in this state under the appellation of *British gum.*

Starch is an important article of food, especially when associated as in ordinary meal with albuminous substances. Arrow-root, and the fecula of the *canna coccinea*, are very pure varieties employed as articles of diet; arrow-root is obtained from the *maranta arundinacea*, cultivated in the West Indies; it is with difficulty distinguished from potato-starch. *Tapioca* is prepared from the root of the *iatropha manihot*, being thoroughly purified from its poisonous juice. *Cassava* is the same substance modified while moist by heat. *Sago* is made from the soft central portion of the stem of a palm; and *salep* from the fleshy root of the *orchis mascula.*

Starch from Iceland moss.—The lichen called *cetraria Islandica*, purified by a little cold solution of potash from a bitter principle, yields, when boiled in water, a slimy and nearly colorless liquid, which gelatinizes on cooling, and dries up to a yellowish amorphous mass, which does not dissolve in cold water, but merely softens and swells. A solution of this substance in warm water is not affected by iodine, although the jelly, on the contrary, is rendered blue. It is precipitated by alcohol, acetate of lead and infusion of galls, and is converted by boiling with dilute sulphuric acid into grape-sugar. According to Mulder, lichen starch contains $C_{24}H_{20}O_{20}$. The jelly from certain *algæ*, as that of Ceylon, and the so-called *Carragheen moss*, closely resembles the above.

INULINE.—This substance, which differs from common starch in some important particulars, is found in the root of the *inula helenium*, the *helianthus tuberosus*, the *dahlia*, and several other plants; it may be easily obtained by washing the rasped root on a sieve, and allowing the inuline to settle down from the liquid; or by cutting the root into thin slices, boiling these in water, and filtering while hot; the inuline separates as the solution cools. It is a white, amorphous, tasteless substance, nearly insoluble in cold water, but freely dissolved by the aid of heat; the solution is precipitated by alcohol, but not by acetate of lead or infusion of galls. Iodine communicates a brown color. Inuline has been carefully analyzed by Mr. Parnell, who finds it to contain, when dried at 212°, $C_{24}H_{21}O_{21}$.

GUM.—*Gum Arabic*, which is the produce of an acacia, may be taken as the most perfect type of this class of bodies. In its purest and finest condition, it forms white or slightly yellowish irregular masses, which are destitute of crystalline structure, and break with a smooth conchoidal fracture. It is soluble in cold water, forming a viscid, adhesive, tasteless solution, from which the pure soluble gummy principle, or *arabine*, is precipitated by alcohol, and by subacetate of lead, but not by the neutral acetate. Arabine is composed of $C_{24}H_{22}O_{22}$, and is consequently isomeric with crystallized cane-sugar.

Mucilage, so abundant in linseed, in the roots of the mallow, and in other plants, differs in some respect from the foregoing, although it agrees in the property of dissolving in cold water. The solution is less transparent than that of gum, and is precipitated by neutral acetate of lead.

Gum-tragacanth is chiefly composed of a substance to which the name *bassorine* has been given, and which refuses to dissolve in water, merely softening and assuming a gelatinous aspect. It is dissolved by caustic alkali. *Cerasine* is the term given to the insoluble portion of the gum of the cherry-tree; it resembles bassorine. The *ropiness* of white wines and saccharine liquids is due to a substance of this kind, which is formed, under peculiar circumstances, from sugar.

Pectine, or the jelly of fruits, seems to be closely allied to the foregoing bodies. It may be extracted from various vegetable juices by precipitation by alcohol. It forms when moist a transparent jelly, imperfectly soluble in water, and tasteless, which dries up to a translucent mass. It is to this substance that the firm consistence of currant and other fruit-jellies is ascribed. In contact with bases, pectine becomes converted into *pectic acid*, which, except that it possesses feeble acid properties, resembles in the closest manner pectine itself. By long boiling with solution of caustic alkali, a further change is produced, and a new acid, the *metapectic*, developed, which does not gelatinize. The salts of these two acids are incapable of crystallizing. Much doubt, too, exists respecting the composition of these bodies, although they are probably isomeric, or only differ in the elements of water; they do not appear, from the analysis yet made, to contain oxygen and hydrogen in the proportion of the equivalent numbers, and consequently scarcely belong to the starch group. Mulder gives for the composition of pectic acid $C_{12}H_8O_{10}$.

LIGNINE; CELLULOSE.—This substance constitutes the fundamental material of the structure of plants; it is employed in the organization of cells, and vessels of all kinds, and forms a large proportion of the solid parts of every vegetable. It must not be confounded with *ligneous* or *woody tissue*, which is in reality cellulose, with other substances superadded, which encrust the walls of the original membranous cells, and confer stiffness and inflexibility. Thus, woody tissue, even when freed as much as possible from coloring matter, and resin by repeated boiling with water and alcohol, yields, on analysis, a result indicating an excess of hydrogen above that required to form water

with the oxygen, besides traces of nitrogen. Pure cellulose, on the other hand, is a ternary compound of carbon and the elements of water, closely allied in composition to starch, if not actually isomeric with that substance.*

The properties of lignine may be conveniently studied in fine linen or cotton, which are almost entirely composed of the body in question, the associated vegetable principles having been removed or destroyed by the variety of treatment to which the fibre has been subjected. Pure lignine is tasteless, insoluble in water and alcohol, and absolutely innutritious; it is not sensibly affected by boiling water, unless it happen to have been derived from a soft or imperfectly developed portion of the plant, in which case it is disintegrated, and rendered pulpy. Dilute acids and alkalis exert but little action on lignine, even at a boiling temperature; strong oil of vitriol converts it, in the cold, into a nearly colorless, adhesive substance, which dissolves in water, and presents the characters of dextrine. This curious and interesting experiment may be conveniently made by very slowly adding concentrated sulphuric acid to half its weight of lint, or linen cut into small shreds, taking care to avoid any rise of temperature, which would be attended with charring or blackening. The mixing is completed by trituration in a mortar, and the whole left to stand a few hours; after which it is rubbed up with water, and warmed, and filtered from a little insoluble matter. The solution may then be neutralized with chalk, and again filtered. The gummy liquid retains lime, partly in the state of sulphate, and partly in combination with a peculiar acid, composed of the elements of sulphuric or hyposulphuric acid, in union with those of the lignine, to which the name sulpholignic acid is given. If the liquid, previous to neutralization, be boiled during three or four hours, and the water replaced as it evaporates, the dextrine becomes entirely changed to grape-sugar. Linen rags may, by these means, be made to furnish more than their own weight of that substance.

Lignine is not colored by iodine.

PRODUCTS ARISING FROM THE ALTERATION OF THE PRECEDING SUBSTANCES BY CHEMICAL AGENTS.

ACTION OF NITRIC ACID.

Oxalic acid. $C_2O_3, HO+2HO$.—This important compound occurs ready formed in several plants, in combination with potash as an acid salt, or with lime. It is now manufactured in large quantities as an article of commerce, by the action of nitric acid on sugar, starch, and dextrine. With the exception of gum and sugar of milk, which yield another product, all the substances comprehended in the saccharine and starch group furnish oxalic acid, as the chief and characteristic result of the long-continued action of moderately strong nitric acid at an elevated temperature.

One part of sugar is gently heated in a retort with 5 parts of nitric acid of sp. gr. 1·42, diluted with twice its weight of water; copious red fumes are disengaged, and the oxidation of the sugar proceeds with violence and rapidity. When the action slackens, heat may be again applied to the vessel, and the liquid concentrated, by distilling off the superfluous nitric acid, until it deposits crystals on cooling. These are drained, re-dissolved in a small quantity of hot water, and the solution set aside to cool. The acid separates from a hot solution in colorless, transparent crystals derived from an oblique rhombic

* Dumas, Chimie appliquée aux Arts, vi. p. 5.

prism, which contain three equivalents of water, one of these being basic and inseparable, except by substitution; the other two may be expelled by a very gentle heat, the crystals crumbling down to a soft white powder, which may be sublimed in great measure without decomposition. The crystallized acid, on the contrary, is decomposed, by a high temperature, into carbonic and formic acids and carbonic oxide, without solid residue.

The crystals of oxalic acid dissolve in 8 parts of water at 60°, and in their own weight, or less, of hot water; they are also soluble in spirit. The aqueous solution has an intensely sour taste, and most powerful acid reaction, and is highly poisonous. The proper antidote is chalk or magnesia. Oxalic acid is decomposed by hot oil of vitriol into a mixture of carbonic oxide and carbonic acid; it is slowly converted into carbonic acid by nitric acid, whence arises a considerable loss in the process of manufacture. The peroxides of lead and manganese effect the same change, becoming reduced to protoxide, which combine with the unaltered acid.

Oxalic acid is formed from sugar by the replacement of the whole of its hydrogen by an equivalent quantity of oxygen.

$$\left.\begin{array}{ll}\text{1 eq. sugar} & = C_{24}H_{18}O_{18} \\ \text{36 eq. oxygen} & = \phantom{C_{24}H_{18}}O_{36}\end{array}\right\} = \left\{\begin{array}{ll}\text{12 eq. oxalic acid} & = C_{24}\phantom{H_{18}}O_{36} \\ \text{18 eq. water} & = \phantom{C_{24}}H_{18}O_{18}\end{array}\right.$$

$$C_{24}H_{18}O_{54} \qquad\qquad C_{24}H_{18}O_{54}$$

The most important salts of oxalic acid are the following:—

Neutral oxalate of potash. KO, C_2O_3+HO.—This is prepared by neutralizing oxalic acid by carbonate of potash. It crystallizes in transparent rhombic prisms, which become opaque and anhydrous by heat, and dissolve in 3 parts of water. Oxalate of potash is often produced when a variety of organic substances are cautiously heated with excess of caustic alkali.

Binoxalate of potash. $KO, 2C_2O_3+3HO$.—Sometimes called *salt of sorrel*, from its occurrence in that plant. This, or the substance next to be mentioned, is found also in the *rumex* and *oxalis acetosella*, and in the garden rhubarb, associated with malic acid. It is easily prepared by dividing a solution of oxalic acid, in hot water, into two equal portions, neutralizing one with carbonate of potash, and adding the other; the salt crystallizes, on cooling, in colorless rhombic prisms. The crystals have a sour taste, and require 40 parts of cold, and 6 of boiling water for solution.

Quadroxalate of potash. $KO, 4C_2O_3+7HO$.—Prepared by a process similar in principle to that last described. The crystals are modified octahedrons, and are less soluble than those of the binoxalate, which the salt in other respects resembles.

Oxalate of soda, NaO, C_2O_3, has but little solubility; a binoxalate exists.

Oxalate of ammonia. NH_4O, C_2O_3+HO.—This beautiful salt is prepared by neutralizing with carbonate of ammonia a hot solution of oxalic acid. It crystallizes in long, colorless, rhombic prisms, which effloresce in dry air from loss of water of crystallization. They are not very soluble in cold water, but freely dissolve by the aid of heat. Oxalate of ammonia is of great value in analytical chemistry, being employed to precipitate lime from its solutions. When oxalate of ammonia is heated in a retort, it is completely decomposed, yielding water, ammonia and carbonate of ammonia, cyanogen and carbonic acid gases, and a small quantity of a peculiar grayish-white sublimate. The latter bears the name of *oxamide*; it is a very remarkable body, and forms the type of a small class of substances containing the elements of an ammoniacal salt, *minus* those of water. Oxamide is composed of $C_2H_2NO_2$, or the elements of 1 eq. amidogen, (NH_2) and 2 eq. carbonic oxide, (C_2O_2). It is insoluble in water and alcohol; when boiled with an

alkali it furnishes an oxalate of the base, and ammonia, which is expelled; and when heated with an acid, it produces an ammoniacal salt.

The *binoxalate* of ammonia is still less soluble than the oxalate.

OXALATE OF LIME. CaO,C_2O_3+2HO.—This compound is formed whenever oxalic acid or an oxalate is added to a soluble salt of lime; it falls as a white powder, which acquires density by boiling, and is but little soluble in dilute hydrochloric acid. Nitric acid dissolves it easily. When dried at 212° it retains an equivalent of water, which may be driven off by a rather higher temperature. Exposed to a red heat in a close vessel, it is converted into carbonate of lime, with escape of carbonic oxide.

The oxalates of *baryta*, *zinc*, *manganese*, *protoxide of iron*, *copper*, *nickel*, and *cobalt*, are nearly insoluble in water; that of *magnesia* is sparingly soluble, and that of the *peroxide of iron* freely soluble. The double *oxalate of chromium and potash*, made by dissolving in hot water 1 part bichromate of potash, 2 parts binoxalate of potash, and 2 parts crystallized oxalic acid, is one of the most beautiful salts known. The crystals appear black by reflected light from the intensity of their color, which is pure deep blue; they are very soluble. The salt contains $3(KO,C_2O_3)+Cr_2O_3,3C_2O_3+6HO$. A corresponding compound containing peroxide of iron has been formed; it crystallizes freely, and has a beautiful green color.

SACCHARIC, OR OXALHYDRIC ACID. $C_{12}H_5O_{11}+5HO$.—This substance was once thought to be identical with malic acid, which is not the case; it is formed by the action of dilute nitric acid on sugar, and is often produced in the preparation of oxalic acid, being, from its superior solubility, found in the mother-liquor from which the oxalic acid has crystallized. It may be made by heating together 1 part sugar, 2 parts nitric acid, and 10 parts water. When the reaction seems terminated, the acid liquid is diluted, neutralized with chalk, and the filtered liquid mixed with acetate of lead. The insoluble saccharate of lead is washed, and decomposed by sulphuretted hydrogen. The acid slowly crystallizes from a solution of sirupy consistence in long colorless needles; it has a sour taste, and forms soluble salts with lime and baryta. When mixed with nitrate of silver, it gives no precipitate, but on the addition of ammonia, a white insoluble substance separates, which is reduced by gently warming the whole to metallic silver, the vessel being lined with a smooth and brilliant coating of the metal. Nitric acid converts the saccharic into oxalic acid. An equivalent of saccharic acid requires for neutralization 5 equivalents of a base.

XYLOIDINE.—When starch is mixed with nitric acid of specific gravity 1·5, it is converted without disengagement of gas into a transparent, colorless jelly, which when put into water yields a white, curdy, insoluble substance; this is the new body *xyloidine*. When dry, it is white and tasteless, insoluble even in boiling water, but freely dissolved by dilute nitric acid, and the solution yields oxalic acid when boiled. Other substances belonging to the same class also yield xyloidine; paper dipped into the strongest nitric acid, quickly plunged into water, and afterwards dried, becomes in great part so changed; it assumes the appearance of parchment, and acquires an extraordinary degree of combustibility. Xyloidine is said to contain $C_6H_4O_4,NO_5$.

[PYROXYLINE; NITRIC CELLULOSE; (*gun cotton*.)—When lignin is immersed in nitric acid of the density 1·52, for a few moments, and then thoroughly washed with a large quantity of water, and dried at a temperature not over 200° F., a remarkably explosive compound is produced, which is *pyroxyline*. An acid of less density may be used by previously mixing with it, its own bulk of sulphuric acid. Pyroxyline presents itself under the nearly unaltered form of the variety of lignin (cotton, paper, &c.,) from which it has been prepared, having acquired only a very perceptible harshness. One hundred parts

of pure lignin yield 176 of pyroxyline. It is white, inodorous, insoluble in water, soluble in acetic ether, and caustic potassa. Dried at 130° it remains unaltered, but at higher temperatures, as 212°—220°, it becomes yellow and friable, exhales the odor of nitric acid, losing about 10 per cent. of its weight in an hour, and sometimes suddenly inflames. It is a good electric, becoming highly charged with positive electricity by friction. Touched with a red-hot or inflamed body, it is immediately consumed without residue. Struck with a hammer, the part struck explodes, and drives off the remainder unconsumed. Its explosive character prevents its analysis by the ordinary means, but its composition has been estimated indirectly to be $C_{24}H_{22}O_{42}N_4$, or one equivalent of anhydrous starch, and four of monohydrated nitric acid, $C_{24}H_{18}O_{18}+4HO NO_5$. Its purity may be ascertained by sulphuric acid or solution of potassa. Lignin dissolved in sulphuric acid of 1·46 to 1·76 soon becomes colored. Pyroxyline under the same circumstances disengages nitric acid vapors and does not communicate any color below 212°. Pyroxyline dissolves in a solution of caustic potassa without color.—R. B.]

MUCIC ACID. $C_{12}H_8O_{14}+2HO$.—Sugar of milk and gum, heated with nitric acid somewhat diluted, furnish, in addition to a small quantity of oxalic acid, a white and nearly insoluble substance called *mucic* acid. It may be easily prepared by heating together in a flask or retort 1 part of milk sugar, or gum, 4 parts of nitric acid and 1 of water; the mucic acid is afterwards collected upon a filter, washed and dried. It has a slightly sour taste, reddens vegetable colors, and forms salts with bases. It requires for solution 66 parts of boiling water Oil of vitriol dissolves it with red color. Mucic acid is decomposed by heat, yielding, among other products, a volatile acid, the *pyromucic*, which is soluble in water, and crystallizes in a form resembling that of benzoic acid. Pyromucic acid is monobasic; it contains $C_{10}H_3O_5+HO$.

SUBERIC ACID, $C_8H_6O_3+HO$, is formed by the action of nitric acid on the peculiar ligneous matter of cork; it much resembles mucic acid, but is more soluble in water.

The following bodies are closely allied in composition to oxalic acid:—

MELLITIC ACID. C_4H_3+HO.—This substance occurs, in combination with alumina, in a very rare mineral called *mellite*, or *honey-stone*, found in deposits of imperfect coal, or *lignite*. It is soluble in water and alcohol, and is crystallizable, forming colorless needles. It combines with bases; the mellitates of the alkalis are soluble and crystallizable; those of the earths and metals proper are mostly insoluble.

RHODIZONIC and CROCONIC ACIDS.—When potassium is heated in a stream of dry carbonic oxide gas, the latter is absorbed in large quantity, and a black porous substance generated, which, when put into water, evolves inflammable gas, and produces a deep red solution containing the potash-salt of a peculiar acid, the *rhodizonic*; by adding alcohol to the liquid, the rhodizonate of potash is precipitated. This and the lead salt are the only two compounds which have been fully examined; the acid itself cannot be isolated. Rhodizonate of potash is composed of C_7O_7+3KO; hence the acid is tribasic.

When solution of rhodizonate of potash is boiled, it becomes orange yellow from decomposition of the acid, and is then found to contain oxalate of potash, free potash, and a salt of an acid to which the term *croconic* is applied. This acid can be isolated; it is yellow, easily crystallizable, and soluble both in water and alcohol. Crystallized croconic acid contains C_5O_4+HO.

THE FERMENTATION OF SUGAR, AND ITS PRODUCTS.

The term fermentation is applied in chemistry to a peculiar metamorphosis of a complex organic substance, by a transposition of its elements under the agency of an external disturbing force, different from ordinary chemical attraction, and more resembling those obscure phenomena of contact already noticed, to which the expression *Katalysis* is sometimes applied. The explanation which Liebig has suggested of the cause and nature of the fermentative change is a very happy one, although of necessity only hypothetical. It has long been known that one of the most indispensable conditions of that process is the presence in the fermenting liquid of certain azotized substances, called *ferments*, whose decomposition proceeds simultaneously with that of the body undergoing metamorphosis. They all belong to the class of albuminous principles, bodies which in a moist condition putrefy and decompose spontaneously. It is imagined that when these substances, in the act of undergoing change, are brought into contact with neutral ternary compounds of small stability, as sugar, the molecular disturbance of the body, already in a state of decomposition, may, be, as it were, propagated to the other, and bring about destruction of the equilibrium of forces to which it owes its being. The complex body, under these circumstances, breaks up into simpler products, which possess greater permanence. Whatever may be the ultimate fate of this ingenious hypothesis, it is certain that decomposing azotized bodies not only do possess very energetic and extraordinary powers of exciting fermentation, but that the *kind* of fermentation set up is, in a great degree, dependent on the phase or stage of decomposition of the ferment.

ALCOHOL; VINOUS FERMENTATION.—A solution of pure sugar, in an open or close vessel, may be preserved unaltered for any length of time; but if putrescible azotized matters be present, in the proper state of decay, the sugar is converted into alcohol, with escape of carbonic acid. Putrid blood, white of egg, or flour-paste, will effect this; by far the most potent alcoholic ferment is, however, to be found in the insoluble, yellowish, viscid matter, deposited from beer in the act of fermentation, called *yeast*. If the sugar be dissolved in a large quantity of water, a due proportion of active yeast added, and the whole maintained at a temperature of 70° or 80°, the change will go on with great rapidity. The gas disengaged will be found to be nearly pure carbonic acid; it is easily collected and examined, as the fermentation, once commenced, proceeds perfectly well in a close vessel, as a large bottle or flask, fitted with a cork and conducting-tube. When the effervescence is at an end, and the liquid has become clear, it will yield alcohol by distillation. Such is the origin of this important compound; it is a product of the metamorphosis of sugar, under the influence of a ferment.

The composition of alcohol is expressed by the formula $C_4H_6O_2$; it is produced by the breaking up of an equivalent of grape-sugar, $C_{24}H_{28}O_{28}$, into 4 eq. of alcohol, 8 of carbonic acid, and 4 of water. It is grape-sugar alone which yields alcohol; the ferment in the experiment above related first converting the cane-sugar into that substance. Milk-sugar may sometimes apparently be made to ferment, but a change into grape-sugar always really precedes the production of alcohol.

The spirit first obtained by distilling a fermented saccharine liquid is very weak, being diluted with a large quantity of water. By a second distillation, in which the first portions of the distilled liquid are collected apart, it may be greatly strengthened; the whole of the water cannot, however, be thus removed. The strongest rectified spirit of wine of commerce has a density of about ·835, and yet contains 13 or 14 per cent. of water. Pure or *absolute* alcohol may be obtained from this by re-distilling it with half its weight of

fresh quicklime. The lime is reduced to coarse powder, and put into a retort; the alcohol is added, and the whole mixed by agitation. The neck of the retort is securely stopped with a cork, and the mixture left for several days. The alcohol is distilled off by the heat of a water-bath.

Pure alcohol is a colorless, limpid liquid, of pungent and agreeable taste and odor; its specific gravity at 60° is ·793, and that of its vapor 1·613. It is very inflammable, burning with a pale bluish flame, free from smoke, and has never been frozen. Alcohol boils at 173°, or perhaps a little below, and it is curious to remark that its volatility is increased by a small quantity of water, although, when more diluted, its boiling-point is progressively raised by each addition of that liquid. In the act of dilution a contraction of volume occurs, and the temperature of the mixture rises many degrees; this takes place not only with pure alcohol, but with rectified spirit. It is miscible with water in all proportions, and, indeed, has a great attraction for the latter, absorbing its vapor from the air, and abstracting the moisture from membranes and other similar substances immersed in it. The solvent powers of alcohol are very extensive; it dissolves a great number of saline compounds, many organic substances, as the vegeto-alkalis, resins, essential oils, and various other bodies; hence its great use in chemical investigations, and in several of the arts.

The strength of commercial spirit is inferred from its density, when free from sugar and other substances added subsequent to distillation; a table exhibiting the proportions of real alcohol and water, in spirits of different densities, will be found at the end of the volume. The excise *proof-spirit* has a sp. gr. of ·918, and contains nearly equal parts of each.

Wine, beer, &c., owe their intoxicating properties to the alcohol they contain, the quantity of which varies very much. Port and sherry, and some other strong wines, contain, according to Mr. Brande, from 19 to 25 per cent. of alcohol, while in the lighter wines of France and Germany, it sometimes falls as low as 12 per cent. Strong ale contains about 10 per cent.; ordinary spirits, as brandy, gin, and whisky, 40 to 50 per cent., or occasionally more. These latter owe their characteristic flavors to certain essential oils, present in very small quantity, either generated in the act of fermentation, or purposely added.

In making wine, the expressed juice of the grape is simply set aside in large vats, where it undergoes spontaneously the necessary change. The vegetable albumen of the juice absorbs oxygen from the air, runs into decomposition, and in that state becomes a ferment to the sugar, which is gradually converted into alcohol. If the sugar be in excess, and the azotized matter deficient, the resulting wine remains sweet; but if, on the other hand, the proportion of sugar be small, and that of albumen large, a *dry* wine is produced. When the fermentation stops, and the liquor becomes clear, it is drawn off from the lees, and transferred to casks, to ripen and improve.

The color of red wine is derived from the skins of the grapes, which in such cases are left in the fermenting liquid. Effervescent wines, as champagne, are bottled before the fermentation is complete; the carbonic acid is disengaged under pressure, and retained in solution in the liquid. The process requires much delicate management.

During the fermentation of the grape-juice, or *must*, a crystalline, stony matter, called *argol*, is deposited. This consists chiefly of acid tartrate of potash, with a little tartrate of lime and coloring matter, and is the source of all the tartaric acid met with in commerce. The salt in question exists in the juice in considerable quantity; it is but sparingly soluble in water, but still less so in dilute alcohol; hence as the fermentation proceeds, and the quantity of spirit increases, it is slowly deposited. The acid of the juice is

thus removed as the sugar disappears. It is this circumstance which renders grape-juice alone fit for making good wine; when that of gooseberries or currants is employed as a substitute, the malic and citric acids which these fruits contain cannot be thus withdrawn. There is, then, no other resource but to add sugar in sufficient quantity to mask and conceal the natural acidity of the liquor. Such wines are necessarily acescent, prone to a second fermentation, and to many persons, at least, very unwholesome.

Beer is a well-known liquor, of great antiquity, prepared from germinated grain, generally barley, and is used in countries where the vine does not flourish. The operation of *malting* is performed by steeping the barley in water until the grains become swollen and soft, then piling it in a heap or *couch*, to favor the elevation of temperature caused by the absorption of oxygen from the air, and afterwards spreading it upon a floor, and turning it over from time to time, to prevent unequal heating. When germination has proceeded far enough, the vitality of the seed is destroyed by kiln-drying. During this process, the curious substance already referred to, diastase, is produced, and a portion of the starch of the grain converted into sugar, and rendered soluble.

In brewing, the crushed malt is infused in water at about 180°, and the mixture left to stand during the space of three hours or more. The easily soluble diastase has thus an opportunity of acting upon the unaltered starch of the grain, and changing the larger portion into dextrine and sugar. The clear liquor, or *wort*, strained from the exhausted malt, is next pumped up, into a copper boiler, and boiled with the requisite quantity of hops for communicating a pleasant bitter flavor, and conferring on the beer the property of keeping without injury. The flowers of the hop contain a bitter, resinous principle called *lupuline*, and an essential oil, both of which are useful.

When the wort has been sufficiently boiled, it is drawn from the copper and cooled, as rapidly as possible, to near the ordinary temperature of the air, in order to avoid an irregular acid fermentation, to which it would otherwise be liable. It is then transferred to the fermenting vessels, which in large breweries are of great capacity, and mixed with a quantity of yeast, the product of a preceding operation, by which the change is speedily induced. This is the most critical part of the whole operation, and one in which the skill and judgment of the brewer are most called into play. The process is in some measure under control by attention to the temperature of the liquid, and the extent to which the change has been carried is easily known by the diminished density, or *attenuation* of the wort. The fermentation is never suffered to run its full course, but is always stopped at a particular point, by separating the yeast, and drawing off the beer into casks. A slow and almost insensible fermentation succeeds, which in time renders the beer stronger and less sweet than when new.

Highly colored beer is made by adding to the malt a small quantity of strongly dried or charred malt, the sugar of which has been changed to caramel. The yeast of beer is a very remarkable substance, and has excited much attention. To the naked eye it is a grayish-yellow, soft solid, nearly insoluble in water, and dries up to a pale brownish mass, which readily putrefies when moistened and becomes offensive. Under the microscope it exhibits a kind of organized appearance, being made up of little transparent globules, which sometimes cohere in clusters or strings, like some of the lowest members of the vegetable kingdom. Whatever may be the real nature of the substance, no doubt can exist that it is formed from the soluble azotized portion of the grain during the fermentive process. No yeast is ever produced in liquids free from azotized matter; that added for the purpose of exciting fermentation in pure sugar, is destroyed, and rendered inert thereby. When yeast is deprived by straining and strong pressure of as much water as possible, it may

be kept in a cool place, with unaltered properties, for a long time; otherwise, it speedily spoils.

The distiller, who prepares spirits from grain, makes his wort, or *wash*, much in the same manner as the brewer; he uses, however, with the malt a large quantity of raw grain, the starch of which suffers conversion into sugar by the diastase of the malt, which is sufficient for the purpose. He does not boil his infusion with hops, but proceeds at once to the fermentation, which he pushes, as far as possible, by large and repeated doses of yeast. Alcohol is manufactured in many cases from potatoes; the potatoes are ground to pulp, mixed with hot water and a little malt, to furnish diastase, made to ferment, and then the fluid portion distilled. The potato-spirit is contaminated by a very offensive volatile oil, again to be mentioned; the crude product from corn contains a substance of a similar kind. The business of the rectifier consists in removing or modifying these volatile oils, and in replacing them by others of a more agreeable character.

In making bread, the vinous fermentation plays an important part; the yeast added to the dough converts the small portion of sugar the meal naturally contains into alcohol and carbonic acid. The gas thus disengaged, forces the tough and adhesive material into bubbles, which are still further expanded by the heat of the oven, which at the same time dissipates the alcohol; hence the light and spongy texture of all good bread. Sometimes carbonate of ammonia is employed with the same view, being completely volatilized by the high temperature of the oven. Bread is now sometimes made by mixing a little hydrochloric acid and carbonate of soda in the dough; if proper proportions be taken, and the whole thoroughly mixed, the operation will no doubt be successful. The use of *leaven* is one of great antiquity; this is merely dough in a state of incipient putrefaction. When mixed with a large quantity of fresh dough, it excites in the latter the alcoholic fermentation, in the same manner as yeast, but less perfectly; it is apt to communicate a disagreeable sour taste and odor.

Lactic acid; lactic acid fermentation.—Azotized albuminous substances, which, in a more advanced state of putrefactive change act as alcohol-ferments, often possess, at an earlier period of decay, the property of inducing an acid fermentation in sugar, the consequenee of which is the conversion of that substance into *lactic acid*. Thus, the azotized matter of malt, when suffered to putrefy in water for a few days, acquires the power of acidifying the sugar which accompanies it, while in a more advanced state of decomposition, it converts, under similar circumstances, the sugar into alcohol. The gluten of grain behaves in the same manner; wheat-flour, made into a paste with water, and left four or five days in a warm situation, becomes a true lactic acid ferment; if left a day or two longer, it changes its character, and then acts like common yeast. Moist animal membranes in a slightly decaying condition, often act energetically in developing lactic acid.

Cane-sugar, probably by previously becoming grape-sugar, and the sugar of milk, both yield lactic acid, the latter, however, most readily, the grape-sugar having a strong tendency towards the alcoholic change. The best method of preparing lactic acid is said to be from milk-sugar. An additional quantity of that substance is dissolved in ordinary milk, which is then set aside in a warm place, until it becomes sour and coagulated. The caseine of the milk absorbs oxygen from the air, runs into putrefaction, and acidifies a portion of the sugar. The lactic acid formed, after a time coagulates and renders insoluble the caseine, and the production of that acid ceases. By carefully neutralizing, however, the free acid by carbonate of soda, the caseine becomes soluble, and resuming its activity, changes a fresh quantity of sugar into lactic acid, which may be also neutralized, and by a sufficient number of repetitions of this pro-

cess, all the sugar of milk present may, in time, be acidified. When this has taken place, the liquid is boiled, filtered, and evaporated to dryness in a water bath. The residue is treated with hot alcohol, which dissolves out the lactate of soda. The alcoholic solution may then be decomposed by the cautious addition of sulphuric acid, which precipitates sulphate of soda, insoluble in spirit. The free acid may, if needful, be neutralized with lime, and the resulting salt purified by recrystallization and the use of animal charcoal, after which it may be decomposed by oxalic acid.

Lactic acid may be extracted from a great variety of liquids containing decomposing organic matter, as *sauerkraut*, a preparation of white cabbage; the sour liquor of the starch-maker, &c. It has been supposed to exist in the blood, urine, and other animal fluids; but this does not seem to be the case, at least in a state of health.

Solution of lactic acid may be concentrated in the vacuum of the air-pump; over a surface of oil of vitriol, until it acquires the aspect of a colorless, sirupy liquid, of sp. gr. 1·215. It has an intensely sour taste and acid reaction; is hygroscopic, and very soluble in water, alcohol, and ether. It forms soluble salts with all the metallic oxides. The sirupy acid contains $C_6H_5O_5+HO$, the water being basic, and susceptible of replacement by a metallic oxide.

When sirupy lactic acid is heated in a retort it undergoes decomposition, yielding, among other products, a white volatile substance, in rhomboidal, shining crystals, which contains $C_6H_4O_4$, or anhydrous lactic acid minus an equivalent of water. When put into cold water, this curious body slowly dissolves, giving a solution of ordinary lactic acid; in hot water it rapidly disappears.

The most important and characteristic of the lactates are those of lime and the oxide of zinc.

Lactate of lime, $CaO,C_6H_5O_5+5HO$, exists ready-formed, to a small extent, in *nux vomica;* it may be prepared from sour milk, or the water in which sauerkraut has been boiled. When pure, it crystallizes in tufts of white needles. It is more freely soluble in hot than in cold water.

Lactate of zinc, $ZnO, C_6H_5O_5+3HO$, is deposited from a hot solution in small brilliant 4-sided prismatic crystals, which are not very soluble in cold water. The *lactate of protoxide of iron* is now used in medicine.

When the expressed juice of the beet is exposed to a temperature of 90° or 100° for a considerable time, the sugar it contains suffers a peculiar kind of fermentation, to which the term *viscous* has been applied. Gases are evolved which contain hydrogen, and when the change appears complete, and the products come to be examined, the sugar is found to have disappeared. Mere traces of alcohol are produced, but in place of that substance, a quantity of lactic acid, mannite, and a mucilaginous substance resembling gum Arabic, and said to be identical with gum in composition.

Pure sugar can be converted into this substance; by boiling yeast or the gluten of wheat in water, dissolving sugar in the filtered solution, and exposing it to a tolerably high temperature, the viscous fermentation is set up, and a large quantity of the gummy principle generated. A little gas is at the same time disengaged, which is a mixture of carbonic acid and hydrogen.*

* To these several modes of fermentation of sugar must yet be added the very curious one quite recently discovered and described by M. Pelouze, in which butyric acid is produced. This will be found under the head of Butyric acid.

PRODUCTS OF THE ACTION OF ACIDS ON ALCOHOL.

ETHER.—When equal weights of rectified spirit and oil of vitriol are mixed in a retort, the latter connected with a good condensing arrangement, and the liquid heated to ebullition, a colorless and highly volatile liquid, long known under the name of *ether*, or *sulphuric ether*, distils over. The process must be stopped as soon as the contents of the retort blacken and froth, otherwise the product will be contaminated with other substances, which then make their appearance. The ether obtained may be mixed with a little caustic potash, and redistilled by a very gentle heat.

Pure ether is a colorless, transparent, fragrant liquid, very thin and mobile. Its sp. gr. at 60° is about ·720; it boils at 96°, under the pressure of the atmosphere, and freezes when exposed to very severe cold. When dropped on the hand it occasions a sharp sensation of cold from its rapid volatilization. Ether is very combustible; it burns with a white flame, generating water and carbonic acid. Although the substance itself is one of the lightest of liquids, its vapor is very heavy, having a density of 2·586. Mixed with oxygen gas, and fired by the electric spark, or otherwise, it explodes with the utmost violence. Preserved in an imperfectly-stopped vessel, ether absorbs oxygen, and becomes acid from the production of acetic acid;—this attraction for oxygen is increased by elevation of temperature. It is decomposed by transmission through a red-hot tube into olefiant gas, light carburetted hydrogen, and a substance yet to be described, *aldehyde*.

Ether is miscible with alcohol in all proportions, but not with water; it dissolves to a small extent in that liquid, 10 parts of water taking up 1 part, or thereabouts, of ether. It may be separated from alcohol, provided the quantity of the latter be not excessive, by an addition of water, and in this manner samples of commercial ether may be conveniently examined. Ether is a solvent for oily and fatty substances generally, and phosphorus to a small extent, a few saline compounds, and some organic principles, but its powers in this respect are much more limited than those of alcohol or water.

Ether is found by analysis to contain C_4H_5O; it resembles in many points an ordinary base in its relations to acids, and is supposed to be the oxide of a salt-basyle, or organic metalloid, not yet isolated, containing C_4H_5.

Table of ether-compounds.

Ethyle, symbol Ae,	C_4H_5
Oxide of ethyle; ether	C_4H_5O
Hydrate of the oxide; alcohol	C_4H_5O,HO
Chloride of ethyle	C_4H_5,Cl
Bromide of ethyle	C_4H_5,Br
Iodide of ethyle	C_4H_5,I
Cyanide of ethyle	C_4H_5,C_2N
Nitrate of oxide of ethyle	C_4H_5O,NO_5
Hyponitrite of oxide of ethyle	C_4H_5O,NO_3
Oxalate of oxide of ethyle	C_4H_5O,C_2O_3
&c. &c.	

The saline, or *quasi*-saline, compounds of ether and its radical are obtained from alcohol, directly or indirectly, by the action of the corresponding acids, as on an ordinary hydrated metallic oxide. Several of these compounds have been long known. No ether-salts of sulphuric or phosphoric acids have yet been formed, from the remarkable tendency of these acids to combine more intimately with the elements of the ether, and generate the compound acids called *sulphovinic* and *phosphovinic*.

The ether salts, like those of the metals, may be divided into haloid and oxygen-acid compounds; they are mostly volatile liquids, in a few cases crystallizable solids, without action on vegetable colors, and not decomposable in the cold by alkaline carbonates. When heated with strong solution of caustic potash or soda, they suffer decomposition, yielding a salt of the alkali or alkaline metal, and hydrate of ether, or alcohol. They are but little soluble in water, but dissolve with great ease in alcohol.

CHLORIDE OF ETHYLE; LIGHT HYDROCHLORIC ETHER. AeCl.—Rectified spirit of wine is saturated with dry hydrochloric acid gas, and the product distilled with very gentle heat; or a mixture of 3 parts oil of vitriol and 2 of alcohol is poured upon 4 parts of dry common salt in a retort, and heat applied; in either case the vapor of the hydrochloric ether should be conducted through a little tepid water in a wash-bottle, and then conveyed into a small receiver surrounded by ice and salt. It is purified from adhering water by contact with a few fragments of fused chloride of calcium. Hydrochloric ether is a thin, colorless, and excessively volatile liquid, of a penetrating, aromatic, and somewhat alliaceous odor. Its sp. gr. is ·874, and it boils at 52°; it is soluble in 10 parts of water, is not decomposed by solution of nitrate of silver, but is quickly resolved into chloride of potassium and alcohol by a hot solution of caustic potash.

BROMIDE OF ETHYLE; HYDROBROMIC ETHER. AeBr.—This is prepared by distilling a mixture of 8 parts bromine, 1 part phosphorus, and 32 parts alcohol. It is a very volatile liquid, of penetrating taste and smell, and superior in density to water.

IODIDE OF ETHYLE; HYDRIODIC ETHER. AeI.—Obtained by the action of iodide of phosphorus on alcohol, or by saturating spirit with hydriodic acid gas, and distilling. Iodide of ethyle is a colorless liquid, of penetrating ethe real odor, having a density of 1·92, and boiling at 160°. It becomes red by contact with air from a commencement of decomposition.

SULPHURET OF ETHYLE. AeS.—Formed by the action of chloride of ethyle upon a solution of the monosulphuret of potassium.* It is colorless, has a disagreeable garlic odor, and boils at 163°.

CYANIDE OF ETHYLE. AeCy.—This is produced when a mixture of sulphovinate of potash and cyanide of potassium, both in a dry state, is slowly heated. It is colorless, has a powerful, offensive alliaceous odor, and a sp. gr. of ·7. It boils at 180°, resists the action of alkalis, but is decomposed by red oxide of mercury.

NITRATE OF OXIDE OF ETHYLE; NITRIC ETHER.—AeO,NO_5.—The nitrate has only recently been obtained; it is prepared by cautiously distilling a mixture of equal weights of alcohol and moderately strong nitric acid, to which a small quantity of nitrate of urea has been added. The action of nitric acid upon alcohol is peculiar;—the facility with which that acid is deoxidized by combustible bodies leads, under ordinary circumstances, to the production of nitrous acid on the one hand, and an oxidized product of alcohol on the other, a *hypo-nitrite* of the oxide of ethyle being generated instead of a nitrate. Mr. Millon has shown that the addition of urea entirely prevents the formation of that substance, and at the same time preserves the spirit from oxidation by undergoing that change in its place, the sole liquid product being the new ether. The experiment is most safely conducted on a small scale, and the distillation must be stopped when seven-eighths of the whole have passed over;—a little water added to the distilled product separates the nitric ether. Nitric ether has a density of 1·112; it is insoluble in water, has an agreeable sweet taste and odor, and is not decomposed by an aqueous solu-

* Regnault, Ann. Chim. et Phys., lxxi. p. 387.

tion of caustic potash, although that substance dissolved in alcohol, attacks it even in the cold with production of nitrate of potash. Its vapor is apt to explode when strongly heated.*

HYPONITRITE OF THE OXIDE OF ETHYLE; HYPONITROUS OR NITROUS ETHER. AeO,NO_3.—Pure hyponitrous ether can only be obtained by the direct action of the acid upon alcohol. 1 part of potato-starch, and 10 parts of nitric acid, are gently heated in a capacious retort or flask, and the vapor of hyponitrous acid thereby evolved conducted into alcohol mixed with half its weight of water, contained in a two-necked bottle, which is to be plunged into cold water, and connected with a good condensing arrangement. All elevation of temperature must be carefully avoided. The product of this operation is a pale yellow volatile liquid, possessing an exceedingly agreeable odor of apples; it boils at 62°, and has a density of ·947. It is decomposed by potash, without darkening, into hyponitrite of the base, and alcohol.†

Hyponitrous ether, but contaminated with aldehyde, may be prepared by the following simple method. Into a tall cylindrical bottle or jar are to be introduced successively 9 parts of alcohol of sp. gr. ·830, 4 parts of water, and 8 parts of strong fuming nitric acid; the two latter are added by means of a long funnel with very narrow orifice, reaching to the bottom of the bottle, so that the contents may form three distinct strata, which slowly mix from the solution of the liquids in each other. The bottle is then loosely stopped and left two or three days in a cool place, after which it is found to contain two layers of liquids, of which the uppermost is the ether. It is purified by rectification. A somewhat similar product may be obtained by carefully distilling a mixture of 3 parts rectified spirit and 2 of nitric acid of 1·28 sp. gr.; the fire must be withdrawn as soon as the liquid boils.

The *sweet spirits of nitre* of pharmacy, prepared by distilling three pounds of alcohol with four ounces of nitric acid, is a solution of hyponitrous ether, aldehyde, and perhaps other substances, in spirit of wine.

CARBONATE OF OXIDE OF ETHYLE; CARBONIC ETHER. AeO, CO_2.—Fragments of potassium or sodium are dropped into oxalic ether as long as gas is disengaged; the brown pasty product is then mixed with water and distilled. The carbonic ether is found floating upon the surface of the water of the receiver as a colorless, limpid liquid of aromatic odor and burning taste. It boils at 259°, and is decomposed by an alcoholic solution of potash into carbonate of that base, and alcohol.‡

Of the ethers of the organic acids, the following are the most important:—

OXALATE OF THE OXIDE OF ETHYLE; OXALIC ETHER. AeO,C_2O_3.—This compound is most easily obtained by distilling together 4 parts binoxalate of potash, 5 parts oil of vitriol, and 4 parts strong alcohol. The distillation may be pushed nearly to dryness, and the receiver kept *warm* to dissipate any ordinary ether that may be formed. The product is mixed with water, by which the oxalic ether is separated from the undecomposed spirit; it is repeatedly washed to remove adhering acid, and re-distilled in a small retort, the first portions being received apart, and rejected.

Pure oxalic ether is a colorless oily liquid, of pleasant aromatic odor, and 1·09 sp. gr. It boils at 363°, is but little soluble in water, and is readily decomposed by caustic alkalis into an oxalate and alcohol. With solution of ammonia in excess, it yields *oxamide* and alcohol. This is the best process for preparing oxamide, which is obtained perfectly white and pure. When dry gaseous ammonia is conducted into a vessel containing oxalic ether, the gas is rapidly absorbed, and a white solid substance produced, which is solu-

* Ann. Chim. et Phys. 3d Series, viii. p. 232.
† Liebig; Geiger's Pharmacie, i. p. 718.
‡ Ettling, Annalen der Pharmacie, xix. p. 17.

ble in hot alcohol, and separates, on cooling, in colorless, transparent, scaly crystals. They dissolve in water, and are both fusible and volatile. The name *oxamethane* is given to this body: it consists of $C_8H_7NO_6$. The same substance is formed when ammonia in small quantity is added to a solution of oxalic ether in alcohol.

ACETATE OF OXIDE OF ETHYLE; ACETIC ETHER. $AeO,C_4H_3O_3$.—Acetic ether is conveniently made by heating together in a retort 3 parts of acetate of potash, 3 parts of strong alcohol, and 2 of oil of vitriol. The distilled product is mixed with water, to separate the alcohol, digested first with a little chalk, and afterwards with fused chloride of calcium, and, lastly, rectified. The pure ether is an exceedingly fragrant, limpid liquid; it has a density of ·890, and boils at 165°. Alkalis decompose it in the usual manner.

FORMIATE OF THE OXIDE OF ETHYLE; FORMIC ETHER. AeO, C_2HO_3. A mixture of 7 parts of dry formiate of soda, 10 of oil of vitriol, and 6 of strong alcohol, is to be subjected to distillation. The formic ether, separated by the addition of water to the distilled product, is agitated with a little magnesia, and left several days in contact with chloride of calcium. Formic ether is colorless, has an aromatic smell, and density of ·915, and boils at 133°. Water dissolves this substance to a small extent.

ŒNANTHIC ETHER.—The aroma possessed by certain wines appears due to the presence of the ether of a peculiar acid, called the *œnanthic*, and which is probably generated during fermentation. When such wines are distilled on the large scale, an oily liquid passes over towards the close of the operation, which consists, in great measure, of the crude ether; it may be purified by agitation with solution of carbonate of potash, freed from water by a few fragments of chloride of calcium, and redistilled. Œnanthic ether is a thin, colorless liquid, having a powerful and almost intoxicating vinous odor; it has a density of ·862, boils at 410°, and is but sparingly soluble in water, although, like the compound ethers in general, it dissolves with facility in alcohol. It contains $C_{18}H_{18}O_3$, or $AeO, C_{14}H_{13}O_2$. The density of its vapor is 10·5.

A hot solution of caustic potash instantly decomposes œnanthic ether; alcohol distils over, and œnanthate of potash remains in the retort; the latter is readily decomposed by warm dilute sulphuric acid, with liberation of œnanthic acid. Purified by repeated washing with hot water, œnanthic acid presents the appearance of a colorless, inodorous oil, which at 55° becomes a soft solid, like butter. It reddens litmus-paper, and dissolves easily in solutions of the alkaline carbonates, and in spirit, and very much resembles the fatty acids, to be hereafter described, the product of saponification. The acid thus obtained is a hydrate, composed of $C_{14}H_{13}O_2+HO$. By distillation, this water is abandoned, and anhydrous acid passes over, containing $C_{14}H_{13}O_2$. Œnanthic ether may be reproduced by distilling a mixture of 5 parts sulphovinate of potash, and 1 part hydrated œnanthic acid.*

CHLOROCARBONIC ETHER.—Although the constitution of this substance is doubtful, it may be here described. Absolute alcohol is introduced into a glass globe containing chlorocarbonic acid (phosgene gas); the gas is absorbed in large quantity, and a yellowish liquid produced, from which water separates the chlorocarbonic ether. When freed from water by chloride of calcium, and from adhering acid by rectification from litharge, it forms a thin, colorless, neutral liquid, which burns with a green flame. Its density is 1·133; it boils at 202°. The vapor, mixed with a large quantity of air, has an agreeable odor, but when nearly pure, is extremely suffocating. It contains $C_6H_5ClO_4$. The density of the vapor is 3·82.

* Liebig and Pelouze, Ann. Chim. et Phys., lxiii. p. 113.

The action of ammonia, gaseous or liquid, upon this substance, gives rise to a very curious product, called by M. Dumas *urethane;* sal-ammoniac is at the same time formed. Urethane is a white, solid, crystallizable body, fusible below 212°, and distilling unchanged, when in a dry state, at about 356°; if moisture be present, it is decomposed, with evolution of ammonia. Water dissolves this substance very easily; the solution is not affected by nitrate of silver, and yields, by spontaneous evaporation, large and distinct crystals. It contains $C_6H_7NO_4$, or the elements of carbonic ether and *urea*,—whence the name.*

COMPOUND ACIDS CONTAINING THE ELEMENTS OF ETHER.

Sulphovinic acid. $C_4H_5O, 2SO_3+HO$.—Strong rectified spirit of wine is mixed with an equal weight of concentrated sulphuric acid, as in the ordinary preparation of ether; the mixture is heated to its boiling point, and then left to cool. When cold, it is diluted with a large quantity of water, and neutralized with chalk; much sulphate of lime is produced. The mass is placed upon a cloth filter, drained, and pressed; the clear solution is evaporated to a small bulk by the heat of a warm-bath, filtered from a little sulphate, and left to crystallize; the product is *sulphovinate of lime*, in beautiful, colorless, transparent crystals, containing $CaO+C_4H_5O, 2SO_3+2HO$. They dissolve in an equal weight of cold water, and effloresce in a dry atmosphere.

A similar salt, containing baryta, $BaO+C_4H_5O, 2SO_3+2HO$, equally soluble, and still more beautiful, may be produced by substituting, in the above process, carbonate of baryta for chalk; from this substance the hydrated acid may be procured by exactly precipitating the base by dilute sulphuric acid, and evaporating the filtered solution, in vacuo, at the temperature of the air. It forms a sour, sirupy liquid, in which sulphuric acid cannot be recognized, and is very easily decomposed by heat, and even by long exposure in the vacuum of the air-pump. All the sulphovinates are soluble; the solutions are decomposed by ebullition. The lead-salt resembles the barytic compound. That of potash, easily made by decomposing sulphovinate of lime by carbonate of potash, is anhydrous; it is permanent in the air, very soluble, and crystallizes well.

Sulphovinate of potash, distilled with concentrated sulphuric acid, gives ether; with dilute sulphuric acid, alcohol; and with strong acetic acid, acetic ether. Heated with hydrate of lime or baryta, the sulphovinates yield a sulphate of the base, and alcohol.

Phosphovinic acid. C_4H_5O, PO_5+2HO.—This acid is bibasic. The baryta-salt is prepared by heating to 180° a mixture of equal weights of strong alcohol and sirupy phosphoric acid, diluting this mixture, after the lapse of 24 hours, with water, and neutralizing by carbonate of baryta. The solution of phosphovinate, separated by filtration from the insoluble phosphate, is evaporated at a moderate temperature. The salt crystallizes in brilliant hexagonal plates, which have a pearly lustre, and are more soluble in cold than in hot water; it dissolves in 15 parts of water at 68°. The crystals contain $2BaO+C_4H_5O, PO_5+12HO$. From this substance the hydrated acid may be obtained, by precipitating the baryta by dilute sulphuric acid, and evaporating the filtered liquid in the vacuum of the air-pump; it forms a colorless, sirupy liquid of intensely sour taste, which sometimes exhibits appearances of crystallization. It is very soluble in water, alcohol, and ether, and easily decomposed by heat when in a concentrated state.

* Ann. Chim. et Phys., liv. p. 225.

The phosphovinates of lime, silver, and lead, possess but little solubility; those of the alkalis, magnesia and strontia, are freely soluble.

Oxalovinic acid. $C_4H_5O, 2C_2O_3+HO$. Oxalic ether is dissolved in anhydrous alcohol, and enough alcoholic solution of caustic potash added to neutralize one-half of the oxalic acid present, whereupon the potash-salt of the new acid precipitates in the form of crystalline scales, insoluble in alcohol, but easily dissolved by water. The free acid is obtained as a sour and exceedingly instable liquid by the addition of hydrofluosilicic acid to a solution of the preceding salt in dilute alcohol. It forms with baryta a very soluble salt.

Another, and a different view, is very frequently taken of the substances just described, and of many analogous compounds. The sulphovinates, phosphovinates, &c., are supposed to possess a constitution resembling that of ordinary double salts, one of the bases being a metallic oxide, and the second ether. Thus, anhydrous sulphovinate of baryta, is written $BaO, SO_3+C_4H_5O, SO_3$, or double sulphate of baryta and ether; hydrated sulphovinic acid is $HO, SO_3+C_4H_5O, SO_3$, or bisulphate of ether. There are, however, grave objections against this mode of viewing the subject; in every true double salt the characters both of acid and bases remain unchanged; alum gives the reactions of sulphuric acid, of alumina, and of potash, while in sulphovinic acid or a sulphovinate, not a trace of sulphuric acid can be detected by any method short of actual decomposition by heat, or otherwise. If sulphovinate of baryta contain sulphate of baryta ready formed, it is very difficult to understand how that salt can be decomposed by an addition of sulphuric acid. The student must, however, bear in mind that *all* views of the constitution of complex organic compounds must, of necessity, be to a great extent hypothetical, and liable to constant alteration with the progress of science.

Products of Decomposition of Sulphovinic Acid by Heat.

A solution of sulphovinic acid, or, what is equivalent to it, a mixture, in due proportions, of oil of vitriol and strong alcohol, undergoes decomposition when heated, yielding products which differ with the temperature to which the liquid is subjected. The cause of the decomposition is to be traced to the instability of the compound itself, and to the basic power of water, and the attraction of the latter for sulphuric acid, in virtue of which it determines the production of that substance, and liberates the elements of the ether.

When the sulphovinic acid is so far diluted as to boil at 260° or below, or when a temperature not exceeding this is applied to a stronger solution by the aid of a liquid bath, the compound acid is resolved into sulphuric acid, which remains behind in the retort or distillatory vessel, while alcohol, and mere traces of ether, are volatilized.

An acid whose boiling-point lies between 260° and 310°, is decomposed, by ebullition, into hydrated sulphuric acid and ether, which is accompanied by small quantities of alcohol.

Lastly, when, by the addition of a large quantity of oil of vitriol, the boiling-point of the mixture is made to rise to 320° and above, the production of ether diminishes, and other substances begin to make their appearance, of which the most remarkable is olefiant gas. The mixture in the retort blackens, sulphurous acid and carbonic acid are disengaged, a yellow, oily, aromatic liquid passes over, and a coaly residue is left, which contains sulphur. The chief and characteristic product is the olefiant gas; the others may be

considered the result of secondary actions. The three modes of decomposition may be thus contrasted:—

Below 260°—$C_4H_5O, 2SO_3 + HO$ and $2HO$ $= C_4H_5O + HO$ and $2SO_3$ HO

260°—310°—$C_4H_5O, 2SO_3 + HO$ and HO $= C_4H_5O$ and $2SO_3$ HO

Above 320°—$C_4H_5O, 2SO_3 + HO$ . . . $= C_4H_4$ and $2SO_3$ HO

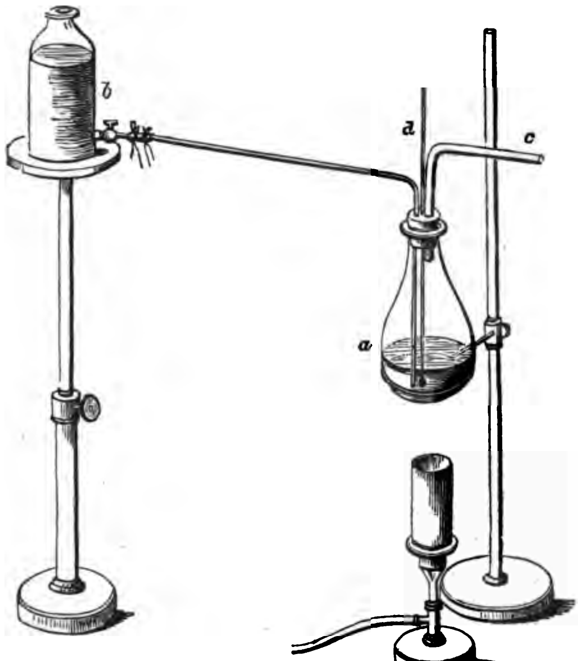
The ether-producing temperature is thus seen to be circumscribed within narrow limits; in the old process, however, in which a mixture of equal weights of alcohol and sulphuric acid is subjected to distillation, these conditions can be but partially complied with. At first the temperature of the mixture is too low to yield ether in any quantity, and towards the end of the process, long before all the sulphovinic acid has been decomposed, it becomes too high, so that olefiant gas, and its accompanying products, appear instead. The remedy to this inconvenience consists in restraining the temperature of ebullition of the mixture within its proper bounds by the introduction of a constant supply of alcohol, to combine with the liberated sulphuric acid, and reproduce the sulphovinic acid as fast as it becomes destroyed. The improved, or *continuous* ether-process, in which the same acid is made to etherify an almost indefinite quantity of spirit, may be thus elegantly conducted upon a small scale.

A wide-necked flask is fitted with a sound cork, perforated by three apertures, one of which is destined to receive a thermometer, with the graduation on the stem; a second, the vertical portion of a long narrow tube, terminating in an orifice of about $\frac{1}{20}$th of an inch in diameter; and the third, a wide bent tube, connected with the condenser, to carry off the volatilized products. A mixture is made of 8 parts by weight of concentrated sulphuric acid, and 5 parts of rectified spirit of wine, of about ·834 sp. gr. This is introduced into the flask, and heated by a lamp. The liquid soon boils, and the thermometer very shortly indicates a temperature of 300°; when this happens, alcohol of the above density is suffered slowly to enter by the narrow tube, which is put into communication with a reservoir of that liquid, consisting of a large bottle, perforated by a hole near the bottom, and furnished with a small brass stop-cock, fitted by a cork; the stop-cock is secured to the end of the long tube by a caoutchouc connecter, tied, as usual, with silk cord. As the tube passes nearly to the bottom of the flask, the alcohol gets thoroughly mixed with the acid liquid, the hydrostatic pressure of the fluid column being sufficient to ensure the regularity of the flow; the quantity is easily adjusted by the aid of the stop-cock. For condensation, a Liebig's condenser may be used, supplied with ice-cold water. The arrangement is figured on the page next following.

The intensity of the heat, and the supply of alcohol, must be so adjusted that the thermometer may remain at 300°, or as near that temperature as possible, while the contents of the flask are maintained in a state of *rapid and violent ebullition*—a point of essential importance. Ether and water distil over together, and collect in the receiver, forming two distinct strata; the mixture slowly blackens, from some slight secondary action of the acid upon the spirit, or upon the impurities in the latter, but retains, after many hours' ebullition, its etherifying powers unimpaired. The acid, however, slowly volatilizes, partly in the state of *oil of wine*, and the quantity of liquid in the flask is found, after the lapse of a considerable interval, sensibly diminished. This loss of acid constitutes the only limit of the duration of the process, which might otherwise be continued indefinitely.

On the large scale, the flask may be replaced by a vessel of lead, the tubes being also of the same metal; the stem of the thermometer may be made to pass air-tight through the cover, and heat may, perhaps, be advantageously

Fig. 157.*



applied by high-pressure steam, or hot oil, circulating in a spiral of metal tube, immersed in the mixture of acid and spirit.

The crude ether is to be separated from the water on which it floats, agitated with a little solution of caustic potash, and re-distilled by the heat of warm water. The aqueous portion, treated with an alkaline solution, and distilled, yields alcohol, containing a little ether. Sometimes the spontaneous separation before mentioned does not occur, from the accidental presence of a larger quantity than usual of undecomposed alcohol; the addition of a little water, however, always suffices to determine it.

Heavy oil of wine.—When a mixture of 2½ parts of concentrated sulphuric acid, and 1 part of rectified spirit of wine, of ·833 sp. gr. is subjected to distillation, a little ether comes over, but is quickly succeeded by a yellowish,

* Fig. 157 Apparatus for the preparation of ether:—*a*. Flask containing the mixture, oil of vitriol and alcohol. *b*. Reservoir, with stop-cock, for supplying a constant stream of alcohol. *c*. Wide bent tube connected with the condenser for conveying away the vapors. *d*. Thermometer for regulating the temperature of the boiling liquid.

oily liquid, which may be freed from sulphurous acid by agitation with water, and from ether and undecomposed alcohol by exposure in the vacuum of the air-pump, besides two open capsules, the one containing hydrate of potash, and the other concentrated sulphuric acid. This substance may be prepared in larger quantity by the destructive distillation of dry sulphovinate of lime; alcohol, oil of wine, and a small quantity of an exceedingly volatile liquid, yet imperfectly examined, are produced. Pure oil of wine is colorless, or greenish, of an oily consistence, and heavier than water; it has an aromatic taste, and an odor resembling that of peppermint. Its boiling-point is tolerably high. It is soluble in alcohol and ether, but scarcely so in water. By analysis, it is found to contain $C_8H_9O, 2SO_3$, or perhaps C_4H_4, SO_3—C_4H_5O, SO_3; that is, neutral sulphate of ether, in combination with the sulphate of a hydro-carbon, *etherole*.

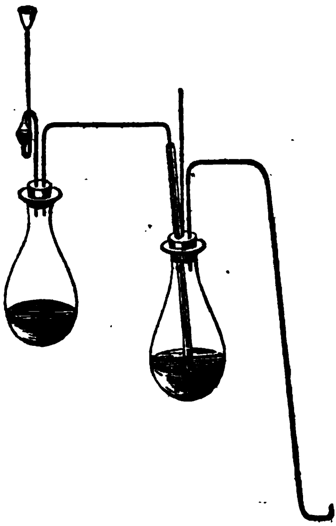
In contact with boiling water, oil of wine is resolved into sulphovinic acid, and a volatile liquid, known by the name of *light*, or *sweet oil of wine;* with an alkaline solution, this effect is produced with even greater facility. Light oil of wine, left in a cool place for several days, deposits crystals of a white solid matter, which is tasteless, and has but little odor; it is called *etherine*. The fluid residual portion is yellowish, oily, and lighter than water; it has a high boiling-point, solidifies at a very low temperature, and is freely soluble in alcohol and ether; it bears the name of *etherole*. Both etherole and etherine have the same composition, namely C_4H_4, and are consequently isomeric with olefiant gas.*

Olefiant gas.—This substance may also be advantageously prepared on the principle described, by restraining the temperature within certain bounds, and preventing the charring and destruction of the alcohol, which always occurs in the old process, and which, at the same time, lead to the production of sulphurous and carbonic acids, which contaminate the gas.

If the vapor of alcohol be passed into somewhat diluted sulphuric acid, maintained at a boiling heat, it is absorbed with production of sulphovinic acid, which is shortly afterwards decomposed into water and olefiant gas. The process is thus conducted:—A wide-necked flask, containing rectified spirit of wine, is fitted with a cork, through which pass an ordinary safety-tube, with a little water, and a bent glass tube, intended to convey the vapor of the spirit into the acid. The latter must be of such strength, as to have a boiling-point between 320° and 330°; it is prepared by diluting strong oil of vitriol with rather less than half its weight of water. The acid is placed in a second and larger flask, also closed by a cork, into which are inserted two tubes, and a thermometer. The first is a piece of straight tube, wide enough to allow the tube conveying the alcohol-vapor to pass freely down it, and dipping a little way into the acid; the second is a narrow bent tube, the extremity of which is immersed in the water of the pneumatic trough. Both flasks are heated; and as soon as it is seen that the acid is in a state of tranquil ebullition, while the thermometer marks the temperature above mentioned, the spirit is made to boil, and its vapor carried into the acid, which very soon begins to evolve olefiant gas and vapor of water, accompanied by a little ether and oil of wine, but no sulphurous acid. The acid liquid does not blacken, and the experiment may be carried on as long as may be desired. This is a very elegant and instructive, although somewhat troublesome, method of preparing the gas. The essential parts of the apparatus are shown in fig. 158.

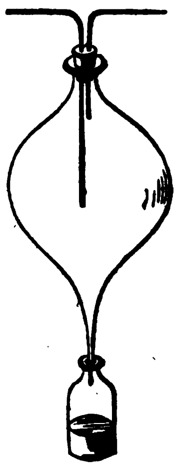
* Sérullas, Ann. Chim. et Phys. xxxix. p. 152; also, Marchand, Id. lxix. p. 259.

Fig. 158.



CHLORIDE OF OLEFIANT GAS; DUTCH LIQUID.—It has long been known that when equal measures of olefiant gas and chlorine are mixed over water, absorption of the mixture takes place, and a yellowish oily liquid is produced, which collects upon the surface of the water, and ultimately sinks to the bottom in drops. It may be easily prepared, in quantity, by causing the two gases to combine in a glass globe, having a narrow neck at the lower part, dipping into a small bottle, destined to receive the product. The two gases are conveyed by separate tubes, and allowed to mix in the globe, the oleflant gas being kept a little in excess. The chlorine should be washed with water, and the olefiant gas passed through strong oil of vitriol, to remove vapor of ether; the presence of sulphurous and carbonic acids is not injurious. Combination takes place very rapidly, and the liquid product trickles down the sides of the globe into the receiver. When a considerable quantity has been collected, it is agitated first with water, and afterwards with concentrated sulphuric acid; it is, lastly, purified by re-distillation. If impure olefiant gas be employed, the crude product contains a large quantity of a substance, called by M. Regnault *chloro-sulphuric acid*, which, on contact with water, is converted, by the decomposition of the latter into sulphuric and hydrochloric acids.

Fig. 159.



Pure Dutch-liquid is a thin, colorless fluid, of agreeably fragrant odor, and sweet taste; it is slightly soluble

in water, and readily so in alcohol and ether. It is heavier than water, and boils when heated to 180°; it is unaffected by oil of vitriol and solid hydrate of potash. When inflamed it burns with a greenish, smoky light. This substance yields, by analysis, $C_4H_4Cl_2$.

When Dutch-liquid is treated with an alcoholic solution of caustic potash, it is slowly resolved into chloride of potassium, which separates, and into a new and exceedingly volatile substance, containing C_4H_3Cl, whose vapor requires to be cooled down to 0° F., before it condenses. At this temperature it forms a limpid, colorless liquid. Chlorine is absorbed by this substance, and a compound produced, which contains $C_4H_3Cl_3$; this is in turn decomposed by an alcoholic solution of hydrate of potash into chloride of potassium, and a new volatile liquid, $C_4H_2Cl_2$.

BROMIDE AND IODIDE OF OLEFIANT GAS. $C_4H_4Br_2$, and $C_4H_4I_2$.—These compounds correspond to Dutch-liquid; they are produced by bringing olefiant gas in contact with bromine and iodine. The bromide is a colorless liquid, of agreeable ethereal odor, and has a density of 2·16; it boils at 265°, and solidifies, when cooled, to near 0°. The iodide is a colorless, crystalline, volatile substance, of penetrating odor; it melts at 174°, resists the action of sulphuric acid, but is decomposed by caustic potash.

PRODUCTS OF THE ACTION OF CHLORINE ON DUTCH LIQUID; CHLORIDES OF CARBON.—Dutch-liquid readily absorbs chlorine gas, and yields several new compounds, produced by the abstraction of successive portions of hydrogen, and its replacement or substitution by equivalent quantities of chlorine.* This regular *substitution* of chlorine, iodine, oxygen, &c., in place of hydrogen, is a phenomenon of constant occurrence in reactions between these bodies, and very many organic compounds. In the present case, three such steps may be traced, giving rise, in each instance, to hydrochloric acid, and a new substance. Two out of the three new products are volatile liquids, containing $C_4H_3Cl_3$ and $C_4H_2Cl_4$; the third, in which the substitution of chlorine for hydrogen is complete, is the *chloride of carbon*, long ago obtained by Mr. Faraday, by putting Dutch-liquid into a vessel of chlorine gas, and exposing the whole to the influence of light.

Perchloride of carbon, C_4Cl_6, is a white, solid, crystalline substance, of aromatic odor, insoluble in water, but easily dissolved by alcohol and ether; it melts at 320°, and boils at a temperature a little above. It burns with difficulty, and is unaffected by both acids and alkalis. It is prepared as above stated.

Protochloride of carbon. C_4Cl_4.—When the vapor of the preceding substance is transmitted through a red-hot porcelain tube filled with fragments of glass or rock-crystal, it is decomposed into free chlorine, and a second chloride of carbon, which condenses in the form of a volatile, colorless liquid, which has a density of 1·55, and boils at 248°. The density of its vapor is 5·82. It resembles in chemical relations the perchloride. A third, or *subchloride of carbon*, C_4Cl_2, is produced when the protochloride is passed many successive times through an ignited porcelain tube; it is a white, volatile, silky substance, soluble in ether.†

COMBUSTIBLE PLATINUM-SALTS OF ZEISE.—A solution of chloride of platinum in alcohol is mixed with a little chloride of potassium dissolved in hydrochloric acid, and the whole digested some hours at a high temperature. The alcohol is distilled off. the acid residue neutralized by carbonate of potash, and left to crystallize. The distilled liquid contains hydrochloric ether and aldehyde.‡ The platinum-salts forms yellow, transparent, prismatic crystals, which become

* Regnault, Ann. Chim. et Phys., lxix. p. 151.
† Idem., lxx. p. 106.
‡ Zeise, Ann. Chim. et Phys., lxiii. p. 411.

opaque on heating from loss of water; when introduced into the flame of a spirit-lamp, the salt burns vividly, leaving metallic platinum. It is soluble in 5 parts of warm water. When dried at 212°, this substance contains Pt_2Cl_2 $C_4H_4 + KCl$. Corresponding compounds, containing $Pt_2Cl_2, C_4H_4 + NaCl$, and $Pt_2Cl_2, C_4H_4 + NH_4Cl$, are known to exist.

The chloride of potassium can be separated from the above compound by the cautious addition of chloride of platinum; the filtered solution yields by evaporation in vacuo a yellow, gummy, acid mass. The solution is slowly decomposed in the cold, and rapidly at a boiling heat, with separation of a black precipitate. These compounds are of uncertain constitution.

PRODUCTS OF THE ACTION OF ANHYDROUS SULPHURIC ACID ON ALCOHOL, ETHER, AND OLEFIANT GAS.

When absolute alcohol is made to absorb the vapor of anhydrous sulphuric acid, a white, crystalline, solid substance is produced, fusible at a gentle heat, which, when purified from adhering acid, is found to consist of carbon, hydrogen, and the elements of sulphuric acid, in the relation of the equivalent numbers, or probably C_4H_4, $4SO_3$. To this substance Magnus applies the name *sulphate of carbyle.** A body very similar in appearance and properties, and possibly identical with this, had previously been produced by M. Regnault,† by passing pure and dry olefiant gas over anhydrous sulphuric acid contained in a bent tube.

When the crystals of sulphate of carbyle are dissolved in alcohol, water added, the whole neutralized by carbonate of baryta, and the filtered solution concentrated by a very gentle heat to a small bulk, and then mixed with a quantity of alcohol, a precipitate falls, which consists of baryta, in combination with a peculiar acid closely resembling the sulphovinic, but yet differing in many important particulars. By the cautious addition of dilute sulphuric acid, the base may be withdrawn, and the hydrate of the new acid left in solution; it bears the name of *ethionic acid*, and contains $C_4H_5O,4SO_3 + 2HO$. The ethionates differ completely from the sulphovinates; all are soluble in water, and appear to be anhydrous. Those of lime, baryta, and oxide of lead refuse to crystallize; the ethionates of potash, soda, and ammonia, on the contrary, may readily be obtained in good crystals.

When a solution of ethionic acid is boiled, it is decomposed into sulphuric acid, and a second new acid, the *isethionic*, isomeric with sulphovinic acid. The isethionic acid and its salts are very stable; their solutions may be boiled without decomposition. The isethionates of baryta, lead, copper, potash, soda, and ammonia crystallize with facility, and cannot be confounded with the sulphovinates. The hydrated acid contains $C_4H_5O,2SO_3 + HO$.

The action of anhydrous sulphuric acid on ether seems to be more complex; no crystals are seen to form, and the liquid, when diluted and saturated with carbonate of baryta, yields, in addition to ethionic acid, a peculiar volatile liquid, recognized as *heavy oil of wine.* When the temperature of the ether has not been carefully kept down, a third new compound acid, the *methionic*, is said to be generated. A fourth, termed by M. Regnault *althionic acid*, identical in composition with sulphovinic acid, but distinguishable by its properties from the others, is said to have been procured from the black residue of the preparation of olefiant gas; M. Magnus, however, could only obtain from this source by saturation with carbonate of baryta the ethionate, isethionate, and sulphovinate of that base.

* Ann. Chim. et Phys., lxxii. p. 68.

† Id., lxv. p. 98.

PRODUCTS OF THE ACTION OF CHLORINE ON ALCOHOL, ETHER, AND ITS COMPOUNDS.

CHLORAL.—Perfectly dry chlorine is passed into anhydrous alcohol to saturation; the gas is absorbed in large quantity, and hydrochloric acid abundantly produced. Towards the end of the process the reaction must be aided by heat. When no more hydrochloric acid appears, the current of chlorine is interrupted, and the product agitated with three times its volume of concentrated sulphuric acid; on gently warming this mixture in a water-bath, the impure chloral separates as an oily liquid, which floats on the surface of the acid; it is purified by distillation from fresh oil of vitriol, and afterwards from a small quantity of quicklime, which must be kept completely covered by the liquid, until the end of the operation.

Chloral is a thin, oily, colorless liquid, of peculiar and penetrating odor, which excites tears; it has but little taste. When dropped upon paper, it leaves a greasy stain, which is not, however, permanent. It has a density of 1·502, and boils at 201°. Chloral is freely soluble in water, alcohol, and ether; it forms, with a small quantity of water, a solid, crystalline hydrate; the solution is not affected by nitrate of silver. Caustic baryta and lime decompose the vapor of chloral when heated in it with appearance of ignition; the oxide is converted into chloride, carbon is deposited, and carbonic oxide set free. Solutions of caustic alkalis also decompose it, with production of a formiate of the base, and a new volatile liquid, *Chloroform*. Chloral contains $C_4H\,Cl_3O_2$.

When chloral is preserved for any length of time, even in a vessel hermetically sealed, it undergoes a very extraordinary change; it becomes converted into a solid, white, translucent substance, *insoluble chloral*, possessing exactly the same composition as the liquid itself. The new product is but very slightly soluble in water, alcohol, or ether; when exposed to heat, alone, or in contact with oil of vitriol, it is reconverted into ordinary chloral. Solution of caustic potash resolves it into formic acid and chloroform.* Bromine acts upon alcohol in the same manner as chlorine, and gives rise to a product very similar in properties to the foregoing, called *bromal*, which contains $C_4H\,Br_3O_2$. It forms a crystallizable hydrate with water, and is decomposed by strong alkaline solutions into formic acid and *bromoform*. A corresponding iodine compound probably exists.

Chlorine acts in a different manner upon alcohol which contains water; when very dilute, the principal products are hydrochloric acid and *aldehyde*, the change being one of oxidation at the expense of the water. With strong spirit the reaction is more complex, one of its products being a volatile, oily, colorless liquid, of uncertain composition, long known under the name of *heavy muriatic ether*.

The mode of action of dry chlorine on pure ether, conforms strictly to the law of substitution before-mentioned; the carbon remains intact, while a portion, or the whole of the hydrogen is removed, and its place supplied by an equivalent quantity of chlorine. Ether exposed to a current of the dry gas for a considerable period, the temperature being at first artificially reduced, yields a heavy oily product, having the odor of fennel. This is found by analysis to contain $C_4H_3Cl_2O$, or ether, in which 2 eq. of chlorine have been substituted for 2 eq. of hydrogen. By the further action of chlorine, aided by sunlight, the remaining hydrogen is removed, and a white crystalline solid substance closely resembling perchloride of carbon, produced. This is com-

* See Liebig, Ann. Chim. et Phys., xlix. p. 146; also, Dumas, Id., lvi. p. 113; also, Regnault, Id. lxxi.

posed of C_4Cl_5O. In a substance called *chlorətheral*, C_4H_4ClO, accidentally formed by M. d'Arcet, in the preparation of Dutch-liquid, from the ether-vapor, mixed with the olefiant gas, we have evidently the first member of this series.

With the compound ethers, the same remarkable law is usually followed; the hydrogen of the base is acted upon, and the organic acid, if such be present, escapes alteration. The change is, however, often complicated by the appearance of secondary products. Thus, *chloruretted acetic ether*, a dense oily liquid, very different from common acetic ether, was found to contain, $C_8H_6Cl_2O_4$, or, $C_4H_3Cl_2O+C_4H_3O_3$ (acetic acid;) and *chloruretted formic ether*, $C_6H_4Cl_2O_4$, is clearly equivalent to $C_4H_3Cl_2O+C_2HO_3$ (formic acid.) A most remarkable and interesting set of compounds, due to substitution of this kind, are formed by the action of chlorine on chloride of ethyle, or light hydrochloric ether. When the vapor of this substance is brought into contact with chlorine gas, the two bodies combine to a colorless oily liquid, very like Dutch-liquid, but yet differing from it in several important points; it has, however, precisely the same composition, and its vapor has the same density. By the prolonged action of chlorine, three other compounds are successively obtained, each poorer in hydrogen and richer in chlorine than the preceding, the ultimate product being the well-known chloride of carbon of Mr. Faraday.*

Hydrochloric ether	C_4H_5Cl
Monochloruretted hydrochloric ether	$C_4H_4Cl_2$
Bichloruretted	$C_4H_3Cl_3$
Trichloruretted	$C_4H_2Cl_4$
Quadrichloruretted	C_4HCl_5
Perchloride of carbon	$C_4\ Cl_6$

DERIVATIVES OF ALCOHOL CONTAINING SULPHUR.

MERCAPTAN.—A solution of caustic potash, of 1·28 or 1·3 sp. gr., is saturated with sulphuretted hydrogen, and mixed in a retort with an equal volume of solution of sulphovinate of lime of the same density. The retort is connected with a good condenser, and heat is applied by means of a bath of salt and water. Mercaptan and water distil over together, and are easily separated by a funnel. The product thus obtained is a colorless, limpid liquid, of sp. gr. ·842, but slightly soluble in water, easily miscible, on the contrary, with alcohol. It boils at 97°. The vapor of mercaptan has a most intolerable odor of onions, which adheres to the clothes and person with great obstinancy; it is very inflammable, and burns with a blue flame. Mercaptan contains $C_4H_6S_2$: or alcohol, having sulphur in the place of oxygen.

The peculiar relations of mercaptan to metallic oxides seem to indicate its title to be considered the hydruret of a radical containing $C_4H_5S_2$. When brought into contact with red oxide of mercury, even in the cold, violent reaction ensues,† water is formed, and a white substance is produced, soluble in alcohol, and separating from that liquid in distinct crystals, which contain $Hg+C_4H_5S_2$. This compound is decomposed by sulphuretted hydrogen, sulphuret of mercury being thrown down, and mercaptan reproduced. By adding solutions of the oxides of lead, copper, silver, and gold, to an alcoholic solution of mercaptan, corresponding compounds containing those metals are formed. Caustic potash produces no effect upon mercaptan, but potassium displaces hydrogen, and gives rise to a crystallizable compound soluble in water.

* Malaguti, Ann. Chim. et Phys., lxx. p. 337; also, Regnault, Id. lxxi. p. 353.
† Whence the name, *mercurium captans*.

Xanthic acid.—The elements of ether and those of bisulphuret of carbon combine in presence of an alkali to form a very extraordinary substance, possessing the properties of an oxygen-acid, to which the name *xanthic* is applied, on account of the yellow color of one of its most permanent and characteristic salts,—that of oxide of copper. Hydrate of potash is dissolved in 12 parts of alcohol of ·800 sp. gr.; into this solution bisulphuret of carbon is dropped until it ceases to be dissolved, or until the liquid loses its alkalinity. The whole is then cooled to 0°, when the potash-salt separates in the form of brilliant, slender, colorless prisms, which must be quickly pressed between folds of bibulous paper, and dried in vacuo. It is freely soluble in water and alcohol, but insoluble in ether, and is gradually destroyed by exposure to air by oxidation of a part of the sulphur. Hydrated xanthic acid may be prepared by decomposing the foregoing compound by dilute sulphuric or hydrochloric acid. It is a colorless, oily liquid, heavier than water, of powerful and peculiar odor, and very combustible; it reddens litmus-paper, and ultimately bleaches it. Exposed to gentle heat, it is decomposed into alcohol and bisulphuret of carbon; this happens at a temperature of 75° F. Exposed to the air, or kept beneath the surface of water open to the atmosphere, it becomes covered with a whitish crust, and is gradually destroyed. The xanthates of the alkalis and of baryta are colorless and crystallizable; the lime-salt dries up to a gummy mass; the xanthates of the oxides of zinc, lead, and mercury, are white and but feebly soluble, that of copper is a flocculent, insoluble substance, of beautiful yellow color.

Hydrated xanthic acid contains $C_6H_5S_4O + HO$; or $C_4H_5O, C_2S_4 + HO$.

PRODUCTS OF THE OXIDATION OF ALCOHOL.

When alcohol and ether burn with flame in free air, the products of their combustion are, as with all bodies of like chemical nature, carbonic acid and water. Under peculiar circumstances, however, these substances undergo partial oxidation, in which the hydrogen alone is affected, the carbon remaining untouched. The result is the production of certain compounds, which form a small series, supposed to contain a common radical, to which the name *acetyle* is applied. It is derived from ethyle by the oxidation and removal of 2 eq. of hydrogen.

Table of Acetyle Compounds.

Acetyle (symbol Ac)	C_4H_3
Oxide of acetyle (unknown)	C_4H_3, O
Hydrate of oxide of acetyle; aldehyde	$C_4H_3, O + HO$
Acetylous acid; aldehydic acid	$C_4H_3, O_2 + HO$
Acetylic acid; acetic acid	$C_4H_3, O_3 + HO$

Acetyle and its protoxide are alike hypothetical.

Aldehyde. $C_4H_4O_2$; or $AcO + HO$.—This substance is formed, as already noticed, among other products, when the vapor of ether or alcohol is transmitted through a red-hot tube; also, by the action of chlorine on weak alcohol. It is best prepared by the following process:—6 parts of oil of vitriol are mixed with 4 parts of rectified spirit of wine, and 4 parts of water; this mixture is poured upon 6 parts of powdered oxide of manganese, contained in a capacious retort, in connection with a condenser, cooled by ice-cold water. Gentle heat is applied; and when about 6 parts of liquid have passed over, the process is interrupted.—The distilled product is put into a small retort, with its own weight of chloride of calcium, and re-distilled; this operation is repeated. The aldehyde, still retaining alcohol and other impurities, is mixed with twice its volume of ether, and saturated with dry ammoniacal gas; a

crystalline compound of aldehyde and ammonia separates, which may be washed with a little ether, and dried in the air. From this substance the aldehyde may be separated by distillation in a water-bath, with sulphuric acid, diluted with an equal quantity of water; by careful rectification from chloride of calcium, at a temperature not exceeding 87°, it is obtained pure and anhydrous.*

Aldehyde† is a limpid, colorless liquid, of characteristic ethereal odor, which, when strong, is exceedingly suffocating. It has a density of ·790, boils at 72° F., and mixes, in all proportions, with water, alcohol, and ether; it is neutral to test-paper, but acquires acidity on exposure to air, from the production of acetic acid;—under the influence of platinum-black, this change is very speedy. When a solution of this compound is heated with caustic potash, a remarkable brown, resin-like substance is produced, the so-called *aldehyde-resin.* Gently heated with oxide of silver, it reduces the latter without evolution of gas, the metal being deposited on the inner surface of the vessel as a brilliant and uniform film; the liquid contains aldehydate of silver.

The ammonia-compound above-mentioned forms transparent, colorless crystals, of great beauty; it has a mixed odor of ammonia and turpentine; it dissolves very easily in water, with less facility in alcohol, and with difficulty in ether; it melts at about 170°, and distils unchanged at 212°. Acids decompose it, with production of an ammoniacal salt, and separation of aldehyde. The crystals, which are apt to become yellow, and lose their lustre in the air, contain $C_4H_4O+NH_3$.

When pure aldehyde is long preserved in a closely-stopped vessel, it is sometimes found to undergo spontaneous change into one, and even two isomeric modifications, differing completely in properties from the original compound. In a specimen kept some weeks at 32°, transparent acicular crystals were observed to form in considerable quantity, which, at a temperature little exceeding that of the freezing point of water, melted to a colorless liquid, miscible with water, alcohol, and ether; a few crystals remained, which sublimed without fusion, and were probably composed of the second substance. This new body received the name *elaldehyde;* it was found to be identical in composition with aldehyde, but to differ in properties, and in the density of its vapor; the latter has a sp. gr. of 4·515, while that of aldehyde is only 1·532, or one-third of that number. It refuses to combine with ammonia, is not rendered brown by potash, and is but little affected by solution of silver.

The second modification, or *metaldehyde*, is sometimes produced in pure aldehyde, kept at the common temperature of the air, even in hermetically-sealed tubes; the conditions of its formation are unknown. It forms colorless, transparent, prismatic crystals, which sublime without fusion at a temperature above 212°, and are soluble in alcohol and ether, but not in water. They also were found, by analysis, to have the same composition as aldehyde.‡

ALDEHYDIC ACID. $C_4H_3O_2+HO$.—When solution of aldehydate of silver, obtained by digesting oxide of silver in excess with aldehyde, is precipitated by sulphuretted hydrogen, an acid liquid is obtained, which neutralizes alkalis, and combines with the oxides of the metals. It is very easily decomposed. Aldehydate of silver, mixed with baryta water, gives rise to aldehydate of baryta and oxide of silver; if this precipitate be heated in the liquid, the metal is reduced, and neutral acetate of baryta formed; whence it is inferred that the new acid contains the elements of acetic acid, *minus* an equivalent of oxygen.§

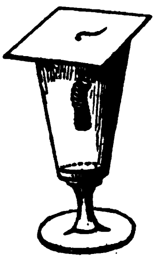
* Liebig, Ann. Chim. et Phys., lix. p. 289.
† *Alcohol dehydrogenatus.*
‡ Fehling, Annalen der Pharmacie, xxvii. p. 319.
§ Liebig, in Geiger's Pharmacie, p. 739.

ACETAL.—This substance is one of the products of the slow oxidation of alcohol-vapor under the influence of platinum-black. Spirit of wine is poured into a large, tall glass jar, to the depth of about an inch, and a shallow capsule, containing slightly-moistened platinum-black, arranged above the surface of the liquid; the jar is loosely covered by a glass plate, and left, during two or three weeks, in a warm situation. At the expiration of that period the liquid will be found highly acid; it is to be neutralized with chalk, and distilled. The volatile product is then treated with chloride of calcium as long as that salt is dissolved; an oily liquid separates, which is a mixture of aldehyde, acetic ether, and acetal. This is transferred to a small retort, fitted with a thermometer, and subjected to distillation. When the temperature rises to 200°, the receiver may be changed, and the pure acetal, which then comes over, collected apart.

Acetal is a thin, colorless liquid, of pungent ethereal odor, soluble in 6 or 7 parts of water, and miscible in all proportions with alcohol. Its density is ·823, and it boils at 203°. Mixed with an alcoholic solution of caustic potash, it is not at first affected, but eventually absorbs oxgen from the air, and gives rise to resin of aldehyde. Its composition is expressed by the formula $C_8H_9O_3$ or perhaps $C_4H_5O+C_4H_4O_2$, a combination of ether and aldehyde.*

When a coil of fine platinum wire is heated to redness, and plunged into a mixture of ether, or alcohol-vapor and atmospheric air, it determines upon its surface the partial combustion of the former, and gives rise to an excessively pungent acrid vapor, which may be condensed to a colorless liquid by suitable means. The heat evolved in the act of oxidation is sufficient to maintain the wire in an incandescent state. The experiment may be made by putting a little ether into an ale-glass, and suspending over it the heated spiral from a card; or by slipping the coil over the wick of a spirit-lamp, so that the greater part may be raised above the cotton; the lamp is supplied with ether or spirit of wine, lighted for a moment, and then blown out. The coil continues to glow in the mixed atmosphere of air and combustible vapor, until the ether is exhausted. This is the *lamp without flame* of Sir H. Davy. A ball of spongy platinum may be substituted for the coil of wire. The condensed liquid contains acetic and formic acids and aldehyde, or aldehydic acid.

Fig. 160.



ACETIC ACID.—Pure alcohol, exposed to the air, or thrown into a vessel of oxygen gas, fails to suffer the slightest change by oxidation; when diluted with water, it remains also unaffected. If, on the other hand, spirit of wine be dropped upon dry platinum-black, the oxygen condensed into the pores of the latter, reacts so powerfully upon the alcohol as to cause its instant inflammation. When the spirit is mixed with a little water, and slowly dropped upon the finely-divided metal, oxidation still takes place, but with less energy, and vapor of acetic acid is abundantly evolved. It is almost unnecessary to add, that the platinum itself undergoes no change in this experiment.

Diluted alcohol, mixed with a little yeast, or almost any azotized organic matter, susceptible of putrefaction, and exposed to the air, speedily becomes oxidized to acetic acid. Acetic acid is thus manufactured in Germany, by suffering such a mixture to flow over wood-shavings, steeped in a little vinegar, contained in a large cylindrical vessel, through which a current of air is made to pass. The greatly extended surface of the liquid expedites the change, which is completed in a few hours. No carbonic acid is produced in this reaction.

* Liebig, in Geiger's Pharmacie; also Ann. Chim. et Phys., lix. p. 313.

The best vinegar is made from wine by spontaneous acidification in a partially-filled cask to which the air has access. Vinegar is first introduced into the empty vessel, and a quantity of wine added; after some days a second portion of wine is poured in, and after similar intervals a third and a fourth. When the whole has become vinegar, a quantity is drawn off equal to that of the wine employed, and the process is recommenced. The temperature of the building is kept up to 86°. Such is the plan adopted at Orleans.* In England vinegar of an inferior description is prepared from a kind of beer made for the purpose. The liquor is exposed to the air in half-empty casks loosely stopped, until acidification is complete. A little sulphuric acid is afterwards added, with a view of checking further decomposition, or *mothering*, by which the product would be spoiled.

There is another source of acetic acid besides the oxidation of alcohol: when dry, hard wood, as oak and beech, is subjected to destructive distillation at a red heat, acetic acid is found among the liquid condensible products of the operation. The distillation is conducted in an iron cylinder of large dimensions, to which a worm or condenser is attached; a sour watery liquid, a quantity of tar, and much inflammable gas pass over, while charcoal of excellent quality remains in the retort. The acid liquid is subjected to distillation, the first portion being collected apart for the sake of a peculiar volatile body, shortly to be described, which it contains. The remainder is saturated with lime, concentrated by evaporation, and mixed with solution of sulphate of soda; sulphate of lime precipitates, while the acetic acid is transferred to the soda. The filtered solution is evaporated to its crystallizing-point; the crystals are drained as much as possible from the dark, tarry mother liquor, and deprived by heat of their combined water. The dry salt is then cautiously fused, by which the last portions of tar are decomposed or expelled; it is then redissolved in water, and recrystallized. Pure acetate of soda, thus obtained, readily yields hydrated acetic acid by distillation with sulphuric acid.

The strongest acetic acid is prepared by distilling finely-powdered anhydrous acetate of soda with three times its weight of concentrated oil of vitriol. The liquid is purified from sulphate of soda accidentally thrown up, by rectification, and then exposed to a low temperature. Crystals of hydrate of acetic acid form in large quantity, which may be drained from the weaker fluid portion, and then suffered to melt. Below 60° this substance forms large, colorless, transparent crystals, which above that temperature fuse to a thin, colorless liquid, of exceedingly pungent and well-known odor; it raises blisters on the skin. It is miscible in all proportions with water, alcohol, and ether, and dissolves camphor and several resins. When diluted it has a pleasant acid taste. The hydrate of acetic acid in the liquid condition has a density of 1·063, and boils at 248°; its vapor is inflammable. Acetic acid forms a great number of exceedingly important salts, all of which are soluble in water; the acetates of silver and mercury are the least soluble.

The hydrate of acetic acid contains—$C_4H_3O_3+HO$; it is formed from alcohol by the substitution of 2 eq. of oxygen for 2 eq. of hydrogen. The water is *basic*, and can be replaced by metallic oxides; anhydrous acetic acid, like very many other bodies of the same class, is unknown in a separate state.

Dilute acetic acid, or distilled vinegar, used in pharmacy, should always be carefully examined for copper and lead; these impurities are contracted from the metallic vessel or condenser sometimes employed in the process. The strength of any sample of acetic acid cannot be safely inferred from its density, but is easily determined by observing the quantity of dry carbonate of soda necessary to saturate a known weight of the liquid.

* Dumas, Chimie appliquée aux Arts, vi. p. 537.

ACETATE OF POTASH. $KO,C_4H_3O_3$.—This salt crystallizes with great difficulty; it is generally met with as a foliated, white, crystalline mass, obtained by neutralizing carbonate of potash by acetic acid, evaporating to dryness, and heating the salt to fusion. The acetate is extremely deliquescent, and soluble in water and alcohol; the solution is usually alkaline, from a little loss of acid by the heat to which it has been subjected. From the alcoholic solution, carbonate of potash is thrown down by a stream of carbonic acid.

ACETATE OF SODA. $NaO,C_4H_3O_3+6HO$.—The mode of preparation of this salt on the large scale has been already described; it forms large, transparent, colorless crystals, derived from a rhombic prism, which are easily rendered anhydrous by heat, effloresce in dry air, and dissolve in 3 parts of cold, and in an equal weight of hot water,—it is also soluble in alcohol. The taste of this substance is cooling and saline. The dry salt undergoes the igneous fusion at 550°, and begins to decompose at 600°.

ACETATE OF AMMONIA; SPIRIT OF MINDERERUS. $NH_4O,C_4H_3O_3$.—The neutral solution obtained by saturating strong acetic acid by carbonate of ammonia, cannot be evaporated without becoming acid from loss of base; the salt passes off in large quantity with the vapor of water. Solid acetate of ammonia is best prepared by distilling a mixture of equal parts acetate of lime and powdered sal ammoniac; chloride of calcium remains in the retort. A saturated solution of the solid salt in hot water, suffered slowly to cool in a close vessel, deposits long slender crystals, which deliquesce in the air. Acetate of ammonia has a sharp and cooling, yet sweet, taste; its solution becomes alkaline on keeping from decomposition of the acid.

The acetates of *lime*, *baryta*, and *strontia* are very soluble, and can be procured in crystals; acetate of *magnesia* crystallizes with difficulty.

ACETATE OF ALUMINA. $Al_2O_3, 3C_4H_3O_3$.—This salt is very soluble in water, and dries up in the vacuum of the air-pump to a gummy mass without trace of crystallization. If foreign salts be present, the solution of the acetate becomes turbid on heating from the separation of a basic compound, which redissolves as the liquid cools. Acetate of alumina is much employed in calico-printing; it is prepared by mixing solutions of acetate of lead and alum, and filtering from the insoluble sulphate of lead. The liquid is thickened with gum or other suitable material, and with it the design is impressed upon the cloth by a wood-block, or by other means. Exposure to a moderate degree of heat drives off the acetic acid, and leaves the alumina in a state capable of entering into combination with the dye-stuff.

Acetate of manganese forms colorless, rhombic prismatic crystals, permanent in the air. *Acetate of protoxide of iron* crystallizes in small greenish-white needles, very prone to oxidation; both salts dissolve freely in water. *Acetate of peroxide of iron* is a dark brownish-red, uncrystallizable liquid of powerful astringent taste. *Acetate of cobalt* forms a violet-colored crystalline, deliquescent mass. The *nickel-salt* separates in green crystals which dissolve in 6 parts of water.

ACETATE OF LEAD. $PbO, C_4H_3O_3+3HO$.—This important salt is prepared on a large scale by dissolving litharge in acetic acid; it may be obtained in colorless, transparent, prismatic crystals, but is generally met with in commerce as a confusedly-crystalline mass, somewhat resembling loaf-sugar. From this circumstance, and from its sweet taste, it is often called *sugar of lead*. The crystals are soluble in about 1½ part of cold water, effloresce in dry air, and melt when gently heated in their water of crystallization; the latter is easily driven off, and the anhydrous salt obtained, which suffers the igneous fusion, and afterwards decomposes, at a higher temperature. Acetate of lead is soluble in alcohol. The watery solution has an intensely sweet, and at the same time astringent, taste, and is not precipitated by ammonia. It is an article of great value to the chemist.

SUBACETATES OF LEAD.—*Sesqui-basic acetate* is produced when the neutral anhydrous salt is so far decomposed by heat as to become converted into a porous white mass, decomposable only at a much higher temperature. It is soluble in water, and separates from the solution evaporated to a sirupy consistence in the form of crystalline scales. It contains $3PbO, 2C_4H_3O_3$. A sub-acetate with 3 eq. of base is obtained by digesting at a moderate heat 7 parts of finely-powdered litharge, 6 parts of acetate of lead, and 30 parts of water. Or, by mixing a cold saturated solution of neutral acetate with a fifth of its volume of caustic ammonia, and leaving the whole some time in a covered vessel; the salt separates in minute needles, which contain $3PbO, C_4H_3O_3+HO$. The solution of sub-acetate prepared by the first method is known in pharmacy under the name of *Goulard water*. A third sub-acetate exists, formed by adding a great excess of ammonia to a solution of acetate of lead, or by digesting acetate of lead with a large quantity of oxide. It is a white, slightly crystalline substance, insoluble in cold, and but little soluble in boiling water. It contains $6PbO, C_4H_3O_3$. The solutions of the sub-acetates of lead have a strong alkaline reaction, and absorb carbonic acid with the greatest avidity, becoming turbid from the precipitation of basic carbonate.

ACETATE OF COPPER. The neutral acetate, $CuO, C_4H_3O_3+HO$, is prepared by dissolving *verdigris* in hot acetic acid, and leaving the filtered solution to cool. It forms beautiful dark-green crystals, which dissolve in 14 parts of cold and 5 parts of boiling water, and are also soluble in alcohol. A solution of this salt, mixed with sugar and heated, yields sub-oxide of copper in the form of minute red octahedral crystals; the residual copper solution is not precipitated by an alkali. Acetate of copper furnishes, by destructive distillation, strong acetic acid, containing acetone, and contaminated with copper. The salt is sometimes called *distilled verdigris*, and is used as a pigment.

SUB-ACETATE OF COPPER.—Common verdigris, made by spreading the marc of grapes upon plates of copper exposed to the air during several weeks, or by substituting, with the same view, pieces of cloth dipped in crude acetic acid, is a mixture of several basic acetates of copper which have a green or blue color. One of these, $3CuO,2C_4H_3O_3+6HO$, is obtained by digesting the powdered verdigris in warm water, and leaving the soluble part to spontaneous evaporation. It forms a blue, crystalline mass, but little soluble in cold water. When boiled, it deposits a brown powder, which is a sub-salt with large excess of base. The green insoluble residue of the verdigris contains $3CuO,C_4H_3O_3+3Ho$; it may be formed by digesting neutral acetate of copper with the hydrated oxide. By ebullition with water it is resolved into neutral acetate and the brown sub-salt.

ACETATE OF SILVER.—$AgO,C_4H_3O_3$, is obtained by mixing acetate of potash with nitrate of silver, and washing the precipitate with cold water to remove the nitrate of potash. It crystallizes from a warm solution in small colorless needles, which have but little solubility in the cold.

Acetate of sub-oxide of mercury forms small scaly crystals, which are as feebly soluble as those of acetate of silver. The salt of the *red oxide of mercury* dissolves with facility.

CHLORACETIC ACID.—When a small quantity of crystallizable acetic acid is introduced into a bottle of dry chlorine gas, and the whole exposed to the direct solar ray for several hours, the interior of the vessel is found coated with a white crystalline substance, which is a mixture of the new product, the chloracetic acid, with a small quantity of oxalic acid. The liquid at the bottom contains the same substances, together with the unaltered acetic acid. Hydrochloric and carbonic acid gases are at the same time produced, together with a suffocating vapor, resembling chloro-carbonic acid. The crystalline matter is dissolved out with a small quantity of water, added to the liquid

contained in the bottle, and the whole placed in the vacuum of the air-pump, besides capsules containing fragments of caustic potash, and concentrated sulphuric acid. The oxalic acid is first deposited, and afterwards the new substance in beautiful rhombic crystals. If the liquid refuses to crystallize, it may be distilled with a little anhydrous phosphoric acid, and then evaporated. The crystals are spread to drain upon bibulous paper, and dried in vacuo.

Chloracetic acid is a colorless and extremely deliquescent substance; it has a faint odor, and a sharp, caustic taste, bleaching the tongue, and destroying the skin; the solution is powerfully acid. At 115° it melts to a clear liquid, and at 390° boils and distils unchanged. The density of the fused acid is 1·617; that of the vapor, which is very irritating, is probably 5·6. The substance contains, according to the analysis of M. Dumas, $C_4H\ O_4Cl_3=C_4Cl_3O_3+HO$, or the elements of hydrated acetic acid from which 3 eq. of hydrogen have been withdrawn, and 3 eq. of chlorine substituted.

Chloracetic acid forms a variety of salts, which have been examined and described; it combines also with ether, and with the ether of wood-spirit. These compounds correspond to the ethers of the other organic acids. *Chloracetate of potash* crystallizes in fibrous, silky needles, which are permanent in the air, and contain $KO,C_4Cl_3O_3+HO$. The *ammoniacal* salt is also crystallizable and neutral; it contains $NH_4O,C_4Cl_3O_3+5HO$. Chloracetate of *silver* is a soluble compound, crystallizing in small grayish scales, which are easily altered by light; it gives, on analysis, $AgO,C_4Cl_3O_3$, and is consequently anhydrous.

When chloracetic acid is boiled with an excess of ammonia, it is decomposed, with the production of chloroform and carbonate of ammonia.

$$C_4H\ Cl_3O_4=C_2H\ Cl_3 \text{ and } C_2O_4.$$

With caustic potash, it yields a smaller quantity of chloroform, chloride of potassium, carbonate and formiate of potash. The chloride and the formiate are secondary products of the reaction of the alkali upon the chloroform.*

ACETONE; PYROACETIC SPIRIT.—When metallic acetates in an anhydrous state are subjected to destructive distillation, they yield, among other products, a peculiar inflammable, volatile liquid, designated by the above names. It is most easily prepared by distilling carefully dried acetate of lead in a large earthen or coated glass retort, by a heat gradually raised to redness; the retort must be connected with a condenser well supplied with cold water. Much gas is evolved, chiefly carbonic acid, and the volatile product, but slightly contaminated with tar, collects in the receiver. The retort is found after the operation to contain minutely-divided metallic lead, which is sometimes pyrophoric. The crude acetone is saturated with carbonate of potash, and afterwards rectified in a water-bath from chloride of calcium. This compound may also be prepared by passing the vapor of strong acetic acid through an iron tube heated to dull redness; the acid is resolved into acetone, carbonic acid, carbonic oxide, and carburetted hydrogen.

Pure acetone is a colorless limpid liquid, of peculiar odor; it has a density of ·792, and boils at 132°; the density of its vapor, 2·022. Acetone is very inflammable, and burns with a bright flame; it is miscible in all proportions with water, alcohol and ether. This substance contains C_3H_3O, and is produced by the resolution of acetic acid into acetone and carbonic acid.

When acetone is distilled with half its volume of Nordhausen sulphuric acid, an oily liquid is obtained, which in a state of purity has a feeble garlic odor. It is lighter than water, and very inflammable. It contains C_3H_2, and is produced by the abstraction of the elements of water from acetone. If

* M. Dumas, Ann. Chim. et Phys., lxxiii. p. 73.

perchloride of phosphorus be dropped into carefully-cooled acetone, and the whole mixed with water, a heavy oily liquid separates, which contains C_6H_5Cl. When this is dissolved in alcohol and mixed with caustic potash, a second oily product results.

This is lighter than water, has an aromatic odor, and contains C_6H_5O.

Dr. Kane has described a number of other compounds formed by the action of acids, and other chemical agents, on acetone, from which the existence of an organic salt-basyle, containing C_6H_5, has been inferred, and to which the name of *mesityle* has been given. Zeise, on the other hand, has shown that by the action of chloride of platinum upon acetone, a yellow crystallizable compound can be obtained, having a composition expressed by the formula $C_6H_5O + PtCl_2$.*

Acetic acid is not the only source of acetone; it may be procured from sugar, starch, and gum by distillation with 8 times their weight of powdered quicklime. The acetone is accompanied by an oily, volatile liquid, separable by water, in which it is insoluble. M. Frémy calls this substance *metacetone;* it contains C_6H_5O, and is consequently isomeric with Dr. Kane's oxide of mesityle.†

When acetate of soda is heated with a great excess of caustic alkali it is converted, as already remarked,‡ into carbonic acid and light carburetted hydrogen, by the reaction of the oxygen of the water of the hydrate upon the carbon of the acid.

$$C_4H_3O_3 \text{ and } HO = C_2O_4 \text{ and } C_2H_4.$$

KAKODYLE AND ITS COMPOUNDS.

The substance long known under the name of *fuming liquor of Cadet*, prepared by distilling a mixture of dry acetate of potash and arsenious acid, has been shown by M. Bunsen to be oxide of an *isoluble* organic basyle, capable of forming a vast number of combinations, displacing other bodies, and being in turn displaced by them, in the same manner as a metal. The investigation of this difficult subject reflects the highest honor on the patience and skill of the discoverer. Kakodyle, so named from its poisonous and offensive nature, contains three elements, viz: carbon, hydrogen, and arsenic.

Table of the most important Kakodyle compounds.

Kakodyle (symbol Kd)	C_4H_6As.
Oxide of kakodyle	KdO.
Chloride of kakodyle	KdCl.
Chloride of kakodyle and copper	$KdCl + Cu_2Cl$.
Oxy-chloride of kakodyle	$3KdCl + KdO$.
Perchloride of kakodyle	$KdCl_3$.
Bromide of kakodyle	KdBr.
Iodide of kakodyle	KdI.
Cyanide of kakodyle	KdCy.
Kakodylic acid	KdO_3.
Kakodylate of silver	AgO,KdO_3.
Kakodylate of kakodyle	KdO,KdO_3.
Sulphuret of kakodyle	KdS.
Sulphuret of kakodyle and copper	$KdS + 3CuS$.
Persulphuret of kakodyle	KdS_3.
Sulphur-salts containing persulphuret of kakodyle	KdS,KdS_3—Au_2S,KdS_3. CuS,KdS_3—PbS,KdS_3.
Seleniuret of kakodyle	KdSe.

* Ann. Chim. et Phys., lxxii. p. 113. † Ann. Chim. et Phys., lix. p. 5. ‡ See p. 132.

OXIDE OF KAKODYLE; CADET'S FUMING LIQUID; ALKARSIN. KdO.—Equal weights of acetate of potash and arsenious acid are intimately mixed, and introduced into a glass retort connected with a condenser and tubulated receiver, cooled by ice: a tube is attached to the receiver to carry away the permanently-gaseous products to some distance from the experimenter. Heat is then applied to the retort, which is gradually increased to redness. At the close of the operation the receiver is found to contain two liquids, besides a quantity of reduced arsenic; the heavier of these is the oxide of kakodyle in a colored and impure condition; the other chiefly consists of water, acetic acid, and acetone. The gas given off during distillation is principally carbonic acid. The crude oxide of kakodyle is repeatedly washed by agitation with water, previously freed from air by boiling, and afterwards re-distilled from hydrate of potash in a vessel filled with pure hydrogen gas. All these operations must be conducted in the open air, and the strictest precautions adopted to avoid the accidental inhalation of the smallest quantity of the vapor or its products.

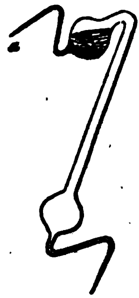
Oxide of kakodyle is a colorless, ethereal liquid of great refractive power; it is much heavier than water, having a density of 1·462. It is very slightly soluble in water, but easily dissolved by alcohol; its boiling-point approaches 300°, and it solidifies to a white crystalline mass at 9°. The odor of this substance is extremely offensive, resembling that of arseniuretted hydrogen; the minutest quantity attacks the eyes and the mucous membrane of the nose; a larger dose is highly dangerous. When exposed to the air, oxide of kakodyle emits a dense, white smoke, becomes heated, and eventually takes fire, burning with a pale flame, and producing carbonic acid, water, and a copious cloud of arsenious acid. It explodes when brought into contact with strong nitric acid, and inflames spontaneously when thrown into chlorine gas. The density of the vapor of this body is about 7·5. Oxide of kakodyle is generated by the reaction of arsenious acid on the elements of acetone, carbonic acid being at the same time formed; the accompanying products are accidental:—

2 eq. acetone, $C_6H_6O_2$ and 1 eq. arsenious acid, AsO_3 = 1 eq. oxide kakodyle, C_4H_6AsO, and 2 eq. carbonic acid, C_2O_4.

CHLORIDE OF KAKODYLE. KdCl.—A dilute alcoholic solution of oxide of kakodyle is cautiously mixed with an equally dilute solution of corrosive sublimate, avoiding an excess of the latter; a white, crystalline, inodorous precipitate falls, containing KdO+2HgCl; when this is distilled with concentrated liquid hydrochloric acid, it yields corrosive sublimate, water, and *chloride of kakodyle*, which distils over. The product is left some time in contact with chloride of calcium and a little quicklime, and then distilled alone in an atmosphere of carbonic acid. The pure chloride is a colorless liquid, which does not fume in the air, but emits a vapor even more fearful in its effects, and more insupportable in odor than that of the oxide. It is heavier than water, and insoluble in that liquid, as also in ether; alcohol, on the other hand, dissolves it with facility. The boiling-point of this compound is a little above 212°; its vapor is colorless, spontaneously inflammable in the air, and has a density of 4·56. Dilute nitric acid dissolves the chloride without change; with the concentrated acid, ignition and explosion occur. Chloride of kakodyle combines with sub-chloride of copper to form a white, insoluble, crystalline double salt, containing $KdCl+Cu_2Cl$, and also with oxide of kakodyle.

KAKODYLE, IN A FREE STATE, may be obtained by the action of metallic zinc, iron, or tin upon the above described compound. Pure and anhydrous chloride of kakodyle is digested for three hours, at a temperature of 212°, with slips of clean metallic zinc contained in a bulb blown upon a glass tube, previously filled with carbonic acid gas, and hermetically sealed. The metal

Fig. 161.



dissolves quietly without evolution of gas. When the action is complete, and the whole cool, the vessel is observed to contain a white saline mass, which on the admission of a little water, dissolves, and liberates a heavy oily liquid, the kakodyle itself. This is rendered quite pure by distillation from a fresh quantity of zinc, the process being conducted in the little apparatus shown in the margin, which is made from a piece of glass tube, and is intended to serve the purpose of both retort and receiver. The zinc is introduced into the upper bulb, and the tube drawn out in the manner represented. The whole is then filled with carbonic acid, and the lower extremity put into communication with a little hand-syringe. On dipping the point *a* into the crude kakodyle and making a slight movement of exhaustion, the liquid is drawn up into the bulb. Both extremities are then sealed in the blow-pipe flame, and after a short digestion at 212° or a little above, the pure kakodyle is distilled off into the lower bulb, which is kept cool. It forms a colorless, transparent, thin liquid, much resembling the oxide in odor, and surpassing that substance in inflammability. When poured into the air, or into oxygen gas, it ignites instantly; the same thing happens with chlorine. With very limited access of air it throws off white fumes, passing into oxide, and eventually into kakodylic acid. Kakodyle boils at 338°, and when cooled to 21° F. crystallizes in large, transparent, square prisms. It combines directly with sulphur and chlorine, and in fact may readily be made to furnish all the compounds previously derived from the oxide. It constitutes the most perfect type of an organic *quasi*-metal which chemistry yet possesses.

Kakodyle is decomposed by a temperature inferior to redness, into metallic arsenic, and a mixture of 2 measures light carburetted hydrogen, and 1 measure olefiant gas.

Chloride of kakodyle forms a *hydrate*, which is thick and viscid, and readily decomposable by chloride of calcium, which withdraws the water. In the preparation of the chloride, and also in other operations, a small quantity of a red amorphous powder is often obtained, called *erytrarsin*. This is insoluble in water, alcohol, ether, and caustic potash, but is gradually oxidized by exposure to the air, with production of arsenious acid. It contains $C_4H_6O_3As_2$.

Iodide of kakodyle. KdI.—This is a thin, yellowish liquid, of offensive odor, and considerable specific gravity, prepared by distilling oxide of kakodyle with strong solution of hydriodic acid. A yellow crystalline substance is at the same time formed, which is an oxy-iodide. *Bromide* and *fluoride* of kakodyle have likewise been obtained and examined.

Sulphuret of kakodyle, KdS, is prepared by distilling chloride of kakodyle with a solution of the double sulphuret of barium and hydrogen. It is a clear, thin, colorless liquid, smelling at once of alkarsin and mercaptan, insoluble in water, and spontaneously inflammable in the air. Its boiling-point is high, but it distils easily with the vapor of water. This substance dissolves sulphur, and generates persulphuret of kakodyle, KdS_3, which is a sulphur-acid, and combines with the sulphurets of gold, copper, bismuth, lead, and antimony.

Cyanide of kakodyle. Kd , C_2N.—The cyanide is easily formed by distilling alkarsin, with strong hydrocyanic acid, or cyanide of mercury. Above 91° F. it is a colorless, ethereal liquid, but below that temperature it crystallizes in colorless four-sided prisms, of beautiful diamond lustre. It boils at about 284°, and is but slightly soluble in water. It requires to be heated

before inflammation occurs. The vapor of this substance is most fearfully poisonous; the atmosphere of a room is said to be so far contaminated by the evaporation of a few grains, as to cause instantaneous numbness of the hands and feet, vertigo, and even unconsciousness.

KAKODYLIC ACID; ALKARGEN. KdO_3.—This is the ultimate product of the action of oxygen at a low temperature upon kakodyle or its oxide; it is best prepared by adding oxide of mercury to that substance, covered with a layer of water, and artificially cooled, until the mixture loses all odor, and afterwards decomposing any kakodylate of mercury that may have been formed by the cautious addition of more alkarsin. The liquid furnishes by evaporation to dryness and solution in alcohol, crystals of the new acid. The sulphuret, and other compounds of kakodyle, yield, by exposure to air, the same substance. Kakodylic acid forms brilliant, colorless, brittle crystals, which have the form of a modified square prism; it is permanent in dry air, but deliquescent in a moist atmosphere. It is very soluble in water and in alcohol, but not in ether; the solution has an acid reaction. When mixed with alkalis and evaporated, a gummy, amorphous mass results. With the oxides of silver and mercury, on the other hand, it yields crystallizable compounds. It unites with oxide of kakodyle, and forms a variety of combinations with metallic salts. Alkargen is exceedingly stable; it is neither effected by red, fuming nitric acid, aqua regia, nor even chromic acid in solution; it may be boiled with these substances without the least change. It is deoxidized, however, by phosphorous acid and protochloride of tin to oxide of kakodyle. Dry hydriodic acid gas decomposes it, with production of water, iodide of kakodyle, and free iodine; hydrochloric acid, under similar circumstances, converts it into a corresponding perchloride, which is solid and crystallizable. Lastly, what is extremely remarkable, this substance is not in the least degree poisonous.

PARAKAKODYLIC OXIDE.—When air is allowed access to a quantity of alkarsin, so slowly that no sensible rise of temperature follows, that body is gradually converted into a thick sirupy liquid, full of crystals of kakodylic acid. Long exposure to air, or the passage of a copious current through the mass, heated to 158°, fails to induce crystallization of the whole. If in this state water be added, everything dissolves, and a solution results which contains kakodylic acid, partly free, and partly in combination with oxide of kakodyle. When this liquid is distilled, water, having the odor of alkarsin, passes over, and afterwards an oily liquid, which is the new compound. Impure kakodylic acid remains in the retort.

Parakakodylic oxide, purified by rectification from caustic baryta, is a colorless, oily liquid, strongly resembling alkarsin itself in odor, relations to solvents, and in the greater number of its reactions. It neither fumes in the air, however, nor takes fire at common temperatures; its vapor, mixed with air, and heated to 190°, explodes with violence. By analysis, it is found to have exactly the same composition as ordinary oxide of kakodyle. It is just possible that, instead of being an isomeric modification of that substance, it may be pure oxide of kakodyle itself, and bear the same relation to the spontaneously inflammable product that *pure* phosphuretted hydrogen does to the gas obtained by the action of water on phosphuret of calcium.*

* See Annalen der Chemie und Pharmacie, xxiv. p. 271; xxvii. p. 148; xxxi. p. 175; xxxvii. p. 1; xlii. p. 14, and xlvi. p. 1.

SECTION II.

SUBSTANCES MORE OR LESS ALLIED TO ALCOHOL.

WOOD-SPIRIT, AND ITS DERIVATIVES.

In the year 1812, Mr. P. Taylor discovered among the liquid products of the destructive distillation of dry wood, a peculiar volatile inflammable liquid, much resembling spirit of wine, to which allusion has already been made. This substance has been shown by M. Dumas* to be really a second alcohol, forming an ether, and a series of compounds, exactly corresponding with those of vinous spirit, and even more complete, in some points, than the latter. Wood-spirit, like ordinary alcohol, is conveniently regarded as the hydrated oxide of a salt-basyle, not yet isolated, containing C_2H_3, called *methyle*.†

Wood-spirit Series.

Methyle (symbol, Me)	C_2H_3
Oxide of methyle	C_2H_3, O
Chloride of methyle	C_2H_3, Cl
Iodide of methyle, &c.	C_2H_3, I .
Wood-spirit	$C_2H_3, O+HO$
Sulphate of oxide of methyle	$C_2H_3, +SO_3$
Nitrate of oxide of methyle, &c.	$C_2H_3, O+NO_5$
Sulphomethylic acid	$C_2H_3O, 2SO_3+HO$
Formic acid	$C_2H\ O_3$
Chloroform	$C_2H\ Cl_3$

Hydrated oxide of methyle; pyroxylic spirit; wood-spirit. $MeO+HO$.—The crude wood-vinegar probably contains about $\frac{1}{100}$th part of this substance, which is separated from the great bulk of the liquid by subjecting the whole to distillation, and collecting apart the first portions which pass over. The acid solution thus obtained is neutralized by hydrate of lime, the clear liquid separated from the oil which floats on the surface, and from the sediment at the bottom of the vessel, and again distilled. A volatile liquid, which burns like weak alcohol, is obtained; this may be strengthened in the same manner as ordinary spirit, by rectification, and ultimately rendered pure and anhydrous, by careful distillation from quicklime, by the heat of a water-bath. Pure wood-spirit is a colorless, thin liquid, of peculiar odor, quite different from that of alcohol, and burning, disagreeable taste; it boils at 152° F., and has a density of ·798 at 68°. The density of its vapor is 1·12. Wood-spirit mixes in all proportions with water, when pure; it dissolves resins and volatile oils as freely as alcohol, and is often substituted for alcohol in various processes in the arts, for which purposes it is prepared on a large scale. It may be burned instead of ordinary spirit, in lamps; the flame is pale-colored,

* MM. Dumas and Péligot. Ann. Chim. et Phys., lviii. p. 5.

† From μηθυ, wine, and υλη, wood; the termination υλη, or *yle*, is very frequently employed in the sense of *matter*, *material*.

like that of alcohol, and deposits no soot. Wood-spirit dissolves caustic baryta; the solution deposits, by evaporation in vacuo, acicular crystals, containing $BaO+MeO, HO$. Like alcohol, it dissolves chloride of calcium in large quantity, and gives rise to a crystalline compound, resembling that formed by alcohol, and containing, according to Dr. Kane, $CaCl+2MeO$, HO.

Oxide of methyle; wood-ether. MeO.—One part of wood-spirit and 4 parts of concentrated sulphuric acid are mixed and exposed to heat in a flask fitted with a perforated cork and bent tube; the liquid slowly blackens, and emits large quantities of gas, which may be passed through a little strong solution of caustic potash, and collected over mercury. This is the *wood-spirit ether*, a permanently gaseous substance, which does not liquefy at the temperature of 3° F. It is colorless, has an ethereal odor, and burns with a pale and feebly luminous flame. Its specific gravity is 1·617. Cold water dissolves about 33 times its volume of this gas, acquiring thereby the characteristic taste and odor of the substance; when boiled, the gas is again liberated. Alcohol, wood-spirit, and concentrated sulphuric acid, dissolve it in still larger quantity.

Chloride of methyle. MeCl.—This compound is most easily prepared by heating a mixture of 2 parts of common salt, 1 of wood-spirit, and 3 of concentrated sulphuric acid; it is a gaseous body, which may be conveniently collected over water, as it is but slightly soluble in that liquid. Chloride of methyle is colorless: it has a peculiar odor and sweetish taste, and burns, when kindled, with a pale flame, greenish towards the edges, like most combustible chlorine-compounds. It has a density of 1·731, and is not liquefied at 0° F. The gas is decomposed by transmission through a red hot tube, with slight deposition of carbon, into hydrochloric acid gas and a carburetted hydrogen, which has been but little examined.

Iodide of methyle, MeI, is a colorless, and feebly combustible liquid, obtained by distilling together 1 part of phosphorus, 8 of iodine, and 12 or 15 of wood-spirit. It is insoluble in water, has a density of 2·237, and boils at 75°. The density of its vapor is 4·883.

Compounds of methyle, with fluorine, cyanogen, and sulphur, have also been obtained.

Sulphate of oxide of methyle. MeO, SO_3.—This interesting substance, to which there is no known analog in the alcohol-series, is readily prepared by distilling 1 part of wood-spirit with 8 or 10 of strong oil of vitriol; the distillation may be carried nearly to dryness. The oleaginous liquid found in the receiver is agitated with water, and purified by rectification from powdered caustic baryta. The product, which is the body sought, is a colorless oily liquid of alliaceous odor, having a density of 1·324, and boiling at 370° F. It is neutral to test-paper, and insoluble in water, but decomposed by that liquid, slowly in the cold, rapidly and with violence at a boiling temperature, into *sulphomethylic acid*, and wood-spirit, which is thus reproduced by hydration of the liberated methylic ether. Anhydrous lime or baryta have no action on this substance; their hydrates, however, and those of potash and soda, decompose it instantly, with a production of a sulphomethylate of the base, and wood-spirit. When neutral sulphate of methyle is heated with common salt, it yields sulphate of soda and chloride of methyle; with cyanide of mercury or potassium, it gives a sulphate of the base, and cyanide of methyle; with dry formiate of soda, sulphate of soda and formiate of methyle. These reactions possess great interest.

Nitrate of the oxide of methyle. MeO, NO_5.—One part of nitrate of potash is introduced into a retort, connected with a tubulated receiver to which is attached a bottle, containing salt and water, cooled by a freezing mixture; a second tube serves to carry off the incondensible gases to a chimney. A

mixture of 1 part of wood-spirit, and 2 of oil of vitriol is made, and immediately poured upon the nitre; re-action commences at once, and requires but little aid from external heat. A small quantity of red vapor is seen to arise, and an ethereal liquid condenses, in great abundance, in the receiver, and also in the bottle. When the process is at an end, the distilled products are mixed, and the heavy oily liquid obtained separated from the water. It is purified by several successive distillations by the heat of a water-bath from a mixture of chloride of calcium and litharge, and, lastly, rectified alone in a retort, furnished with a thermometer passing through the tubulature. The liquid begins to boil at about 140°; the temperature soon rises to 150°, at which point it remains constant; the product is then collected apart, the first and most volatile portions being contaminated with hydrocyanic acid, and other impurities. Even with these precautions, the nitrate of methyle is not quite pure, as the analytical results show. The properties of the substance, however, remove any doubts respecting its real nature.

Nitrate of methyle is colorless, neutral, and of feeble odor; its density is 1·182; it coils at 150°, and burns, when kindled, with a yellow flame. Its vapor has a density of 2·64, and is eminently explosive; when heated in a flask or globe to 300°, or a little above, it explodes with fearful violence; the determination of the density of the vapor is, consequently, an operation of danger. Nitrate of methyle is decomposed by a solution of caustic potash into nitrate of that base, and wood-spirit.

Oxalate of oxide of methyle.—MeO, C_2O_3.—This beautiful and interesting substance is easily prepared by distilling a mixture of equal weights of oxalic acid, wood-spirit, and oil of vitriol. A spirituous liquid collects in the receiver, which, exposed to the air, quickly evaporates, leaving the oxalic methyle-ether in the form of rhombic transparent crystalline plates, which may be purified by pressure between folds of bibulous paper, and re-distilled from a little oxide of lead. The product is colorless, and has the odor of common oxalic ether; it melts at 124°, and boils at 322°. It dissolves freely in alcohol and wood-spirit, and also in water, which, however, rapidly decomposes it, especially when hot, into oxalic acid and wood-spirit. The alkaline hydrates effect the same change even more easily. Solution of ammonia converts it into oxamide and wood-spirit. With dry ammoniacal gas it yields a white, solid substance, which crystallizes from alcohol in pearly cubes; this new body contains $C_6H_5NO_6$, and is designated *oxamethylane*. Many other salts of oxide of methyle have been formed and examined. The *acetate*, $MeO,C_4H_3O_3$, is abundantly obtained by distilling 2 parts of wood-spirit with 1 of crystallizable acetic acid, and 1 of oil of vitriol. It much resembles acetic ether, having a density of ·919, and boiling at 136°; the density of its vapor is 2·563. This compound is isomeric with formic ether.

Formiate of methyle, MeO,C_2HO_3, is prepared by heating in a retort equal weights of sulphate of methyle and formiate of soda. It is very volatile, lighter than water, and is isomeric with hydrate of acetic acid. *Chloro-carbonic methyle-ether* is produced by the action of that gas upon wood-spirit; it is a colorless, thin, heavy, and very volatile liquid, containing $C_4H_3ClO_4$. It yields with dry ammonia a solid crystallizable substance, called *urethylane*.

Sulphomethylic acid.—$MeO,2SO_3+HO$.—Sulphomethylate of barytes is prepared in the same manner as the sulphovinate; 1 part of wood-spirit is slowly mixed with 2 parts of concentrated sulphuric acid, the whole heated to ebullition, and left to cool, after which it is diluted with water and neutralized with carbonate of baryta. The solution is filtered from the insoluble sulphate, and evaporated, first in a water-bath, and afterwards in vacuo to the due degree of concentration. The salt crystallizes in beautiful square colorless tables, containing $BaO+C_2H_3O,2SO_3+2HO$, which effloresce in dry air, and are

very soluble in water. By exactly precipitating the base from this substance by dilute sulphuric acid, and leaving the filtered liquid to evaporate in the air, hydrated sulphomethylic acid may be procured in the form of a sour, sirupy liquid, or as minute acicular crystals, very soluble in water and alcohol. It is very instable, being decomposed by heat in the same manner as sulphovinic acid. *Sulphomethylate of potash* crystallizes in small, nacreous, rhombic tables, which are deliquescent; it contains $KO+C_2H_3O,2SO_3$. The lead-salt is also very soluble.

FORMIC ACID.—As alcohol by oxidation under the influence of finely-divided platinum gives rise to acetic acid, so wood-spirit, under similar circumstances, yields a peculiar acid product, produced by the substitution of 2 eq. of oxygen for 2 eq. of hydrogen, to which the term *formic* is given, from its occurrence in the animal kingdom, in the bodies of ants. The experiment may be easily made by enclosing wood-spirit in a glass jar with a quantity of platinum-black, and allowing moderate access of air; the spirit is gradually converted into formic acid. There is no intermediate product corresponding to aldehyde. Anhydrous formic acid, as in the salts, contains $C_2H\,O_3$, or the elements of 2 eq. carbonic oxide, and 1 eq. water.

Pure hydrate of formic acid, $C_2H\,O_3+HO$, is obtained by the action of sulphuretted hydrogen on dry formiate of lead. The salt, reduced to fine powder, is very gently heated in a glass tube connected with a condensing apparatus, through which a current of dry sulphuretted hydrogen gas is transmitted. It forms a clear, colorless liquid, which fumes slightly in the air, of exceedingly penetrating odor, boiling at about 212°, and crystallizing in large brilliant plates when cooled below 32°. The sp. gr. of the acid is 1·235; it mixes with water in all proportions; the vapor is inflammable, and burns with a blue flame. A second hydrate, containing 2 eq. of water, exists; its density is 1·11, and it boils at 223°. In its concentrated form, this acid is extremely corrosive; it attacks the skin, forming a blister or an ulcer, painful and difficult to heal. A more dilute acid may be prepared by a variety of processes; starch, sugar, and many other organic substances often yield formic acid when heated with oxidizing agents; a convenient method is the following:—1 part of sugar, 3 of peroxide of manganese, and 2 of water are mixed in a very capacious retort, or large metal still; 3 parts of oil of vitriol, diluted with an equal weight of water, are then added, and when the first violent effervescence from the disengagement of carbonic acid has subsided, heat is cautiously applied, and a considerable quantity of liquid distilled over. This is very impure; it contains a volatile oily matter, and some substance which communicates a pungency not proper to formic acid in that dilute state. The acid liquid is neutralized with carbonate of soda, and the resulting formiate purified by crystallization, and if needful, by animal charcoal. From this, or any other of its salts, solution of formic acid may be readily obtained by distillation with dilute sulphuric acid. It has an odor and taste much resembling those of acetic acid, reddens litmus strongly, and decomposes the alkaline carbonates with effervescence.

Formic acid, in quantity, may be extracted from ants by distilling the insects with water, or by simply macerating them in the cold liquid.

Formic acid is readily distinguished from acetic acid by heating it with a little solution of oxide of silver or mercury; the metal is reduced, and precipitates in a pulverulent state, while carbonic acid is extricated; this reaction is sufficiently intelligible. The chloride of mercury is reduced, by the aid of the elements of water, to calomel, carbonic and hydrochloric acids being formed.

The most important salts of formic acid are the following:—*Formiate of soda* crystallizes in rhombic prisms containing 2 eq. of water; it is very

soluble, and is decomposed like the rest of the salts by hot oil of vitriol with evolution of pure carbonic oxide. Fused with many metallic oxides, it causes their reduction. *Formiate of potash* is with difficulty made to crystallize from its great solubility. *Formiate of ammonia* crystallizes in square prisms; it is very soluble, and is decomposed by a high temperature into hydrocyanic acid and water, the elements of which it contains. The salts of *baryta*, *strontia*, *lime*, and *magnesia* form small prismatic crystals, soluble without difficulty. *Formiate of lead* crystallizes in small, diverging, colorless needles, which require for solution 40 parts of cold water. The formiates of *manganese*, *protoxide of iron*, *zinc*, *nickel*, and *cobalt*, are also crystallizable. That of *copper* is very beautiful, constituting bright blue, rhombic prisms of considerable magnitude. Formiate of *silver* is white, but slightly soluble, and decomposed by the least elevation of temperature.

CHLOROFORM.—This substance is produced, as already remarked, when an aqueous solution of caustic alkali is made to act upon chloral. It may be obtained with greater facility by distilling alcohol, wood-spirit, or acetone with a solution of chloride of lime. 1 part of hydrate of lime is suspended in 24 parts of cold water, and chlorine passed through the mixture until nearly the whole lime is dissolved. A little more hydrate is then added to restore the alkaline re-action, the clear liquid mixed with 1 part of alcohol or wood-spirit, and, after an interval of 24 hours, cautiously distilled in a very spacious vessel. A watery liquid containing a little spirit, and a heavy oil collect in the receiver; the latter, which is the chloroform, is agitated with water, digested with chloride of calcium, and rectified in a water-bath. It is a thin, colorless liquid of agreeable ethereal odor, much resembling that of Dutch-liquid, and sweetish taste. Its density is 1·48, and it boils at 141°; the density of its vapor is 4·116. Chloroform is with difficulty kindled, and burns with a greenish flame. It is nearly insoluble in water, and is not affected by concentrated sulphuric acid. Alcoholic solution of potash quickly decomposes it with production of chloride of potassium and formiate of potash.

Chloroform contains $C_2H\,Cl_3$; it is changed to formic acid by the substitution of three eq. of oxygen for the three eq. of chlorine removed by the alkaline metal.

Bromoform, $C_2H\,Br_3$, is a heavy, volatile liquid prepared by a similar process, bromine being substituted in the place of chlorine. It is converted by alkalis into bromide of potassium and formiate of potash. *Iodoform*, $C_2H\,I_3$, is a solid, yellow, crystallizable substance, easily obtained by adding alcoholic solution of potash to tincture of iodine, avoiding excess, evaporating the whole to dryness, and treating the residue with water. Iodoform is nearly insoluble in water, but dissolves in alcohol, and is decomposed by alkalis in the same manner as the preceding compounds.

FORMOMETHYLAL.—This is a product of the distillation of wood-spirit with dilute sulphuric acid and oxide of manganese. The distilled liquid is saturated with potash, by which the new substance is separated as a light oily fluid. When purified by rectification, it is colorless, and of agreeable aromatic odor; it has a density of ·855, boils at 107°, and is completely soluble in three parts of water. It contains $C_3H_4O_2$.

METHYL-MERCAPTAN is prepared by a process similar to that recommended for ordinary mercaptan, sulphomethylate of potash being substituted for the sulphovinate of lime. It is a colorless liquid, of powerful alliaceous odor, and lighter than water; it boils at 68°, and resembles mercaptan in its action on red oxide of mercury.

PRODUCTS OF THE ACTION OF CHLORINE ON THE COMPOUNDS OF METHYLE.—Chlorine acts upon the methylic compounds in a manner strictly in obedience to the law of substitution; the carbon invariably remains intact, and every

proportion of hydrogen removed is replaced by an equivalent quantity of chlorine. Methylic ether and chlorine, in a dry and pure condition, yield a volatile liquid product, containing $C_2H_2Cl\ O$; the experiment is attended with great danger, as the least elevation of temperature gives rise to a violent explosion. This product in its turn furnishes, by the continued action of the gas, a second liquid, containing $C_2H\ Cl_2O$. The whole of the hydrogen is eventually lost, and a third compound, C_2Cl_3O, produced. Even the oxygen may, it seems, be displaced, and a new chloride of carbon, C_2Cl_4, generated.

Chloride of methyle, C_2H_3Cl, in like manner gives rise to three successive products. The first, $C_2H_2Cl_2$, is a new volatile liquid, much resembling chloride of olefiant gas; the second, $C_2H\ Cl_3$, is no other than chloroform; the third is chloride of carbon, C_2Cl_4.* The acetate of methyle, $C_6H_6O_4$, gives $C_6H_4Cl_2O_4$, and $C_6H_3Cl_3O_4$; the other salts are without doubt affected in a similar manner.

Commercial wood-spirit is very frequently contaminated with other substances, some of which are with great difficulty separated. It often contains aldehyde, sometimes acetone, and very frequently a volatile oil, which is precipitated by the addition of water, rendering the whole turbid. A specimen of wood-spirit, from Wattwyl, in Switzerland, was found by Gmelin to contain a volatile liquid, differing in some respects from acetone, to which he gave the term *lignone*. A very similar substance is described by Schweitzer and Weidmann, under the name of xylite.† Lastly, Mr. Scanlan has obtained from wood-spirit a solid, yellow, crystallizable substance, called *eblanine*. It is left behind in the retort when the crude spirit is rectified from lime; it is insoluble in water, sublimes without fusion at 273°, and contains, according to Dr. Gregory, $C_{21}H_9O_4$.

POTATO-OIL, AND ITS DERIVATIVES.

In the manufacture of potato-brandy the crude spirit is found to be contaminated with an acrid volatile oil, which is extremely difficult to separate in a complete manner. Towards the end of the distillation it passes over in considerable quantity; it may be collected apart, agitated with several successive portions of water to withdraw the spirit, with which it is mixed, and re-distilled. This substance exhibits properties indicative of a constitution analogous to that of alcohol; it may be considered as the hydrate of the oxide of a hydrocarbon, called *amyle*, containing $C_{10}H_{11}$.‡ The ether of potato-oil has not yet been obtained; but a variety of other compounds, corresponding in every point to those of ordinary alcohol, have been formed, as will be manifest from an inspection of the following table:—

Amyle (symbol Ayl)	$C_{10}H_{11}$
Amyle-ether (unknown)	$C_{10}H_{11}, O$
Potato-oil,	$C_{10}H_{11}, O+HO$
Chloride of amyle	$C_{10}H_{11}, Cl$
Bromide of amyle	$C_{10}H_{11}, Br$
Iodide of amyle	$C_{10}H_{11}, I$
Acetate of amyle	$C_{10}H_{11}, O+C_4H_3O_3$
Sulphamilic acid	$C_{10}H_{11}O, 2SO_3+HO$
Amilen	$C_{10}H_{10}$
Valerianic acid	$C_{10}H_9O_3$

* Regnault, Ann. Chim. et Phys., lxxi. p. 353.
† Annalen der Chemie und Pharmacie, xxxvi. p. 205.
‡ See Cahours, Ann. Chim. et Phys., lxx. p. 81; and lxxv. p. 193.

HYDRATED OXIDE OF AMYLE; FUSEL-OIL.—AylO+HO.—When pure, this is a thin fluid oil, exhaling a powerful and peculiarly suffocating odor, and leaving a burning taste; it inflames with some difficulty, and then burns with a pure blue flame. Its density is ·818, and boiling-point 262° F. It undergoes little change by contact with air under ordinary circumstances; but when warmed and dropped upon platinum-black, it oxidizes to *valerianic acid*, which bears the same relation to this substance that acetic acid does to ordinary alcohol.

CHLORIDE OF AMYLE.—AylCl.—The chloride is procured by subjecting to distillation equal weights of potato-oil and perchloride of phosphorus, washing the product repeatedly with alkaline water, and rectifying it from chloride of calcium. It is a colorless liquid, of agreeable aromatic odor, insoluble in water, and neutral to test-paper; it boils at 215°, and ignites readily, burning with a flame green at the edges. By the long-continued action of chlorine, aided by powerful sunshine, a new product, or *chloruretted chloride of amyle*, was obtained in the form of a volatile, colorless liquid, smelling like camphor, and containing $C_{10}H_3Cl_9$; the whole of the hydrogen could not, however, be removed.

BROMIDE OF AMYLE, Ayl Br, is a volatile, colorless liquid, heavier than water; its odor its penetrating and alliaceous. The bromide is decomposed by an alcoholic solution of potash with production of bromide of the metal.

IODIDE OF AMYLE, Ayl I, is procured by distilling a mixture of 15 parts of potato-oil, 8 of iodine, and 1 of phosphorus. It is colorless when pure, heavier than water, volatile without decomposition at 248°, and resembles in other respects the bromide; it is partly decomposed by exposure to light.

ACETATE OF OXIDE OF AMYLE.—Ayl O, $C_4H_3O_3$.—This interesting product is easily obtained by submitting to distillation a mixture of 1 part of potato-oil, 2 parts of acetate of potash, and 1 part of concentrated sulphuric acid; it is purified by washing with dilute alkali, and distillation from chloride of calcium. It presents the appearance of a colorless, limpid liquid, which is insoluble in water, soluble in alcohol, boils at 257°, and becomes converted by an alcoholic solution of potash into an acetate of the base, with reproduction of the oil.

SULPHAMILIC ACID.—When equal weights of potato-oil and strong sulphuric acid are mixed, heat is evolved, accompanied by blackening and partial decomposition. The mixture diluted with water and saturated with carbonate of baryta, affords sulphate of that base, and a soluble salt corresponding to the sulphovinate. The latter may be obtained in a crystalline state by gentle evaporation, and purified by re-solution and the use of animal charcoal. It forms small, brilliant, pearly plates, very soluble in water and alcohol, containing $BaO+C_{10}H_{11}O, 2SO_3+HO$. The baryta may be precipitated from the salt by dilute sulphuric acid, and the hydrated sulphamilic acid concentrated by spontaneous evaporation to a syrupy, or even crystalline state; it has an acid and bitter taste, strongly reddens litmus paper, and is decomposed by ebullition into potato-oil and sulphuric acid. The potash-salt forms groups of small radiated needles, very soluble in water. The sulphamilates of lime and oxide of lead are also soluble and crystallizable.

AMILEN.—By the distillation of the potato-oil with anhydrous phosphoric acid, a volatile, colorless, oily liquid is procured, quite different in properties from the original substance. It is lighter than water, boils at 320° or thereabouts, and contains no oxygen. Its composition is represented by the formula $C_{10}H_{10}$; consequently, it not only corresponds to olefiant gas in the alcohol series, but is isomeric with that substance. The vapor, however, has a density of 5·06, which is five times that of olefiant gas, every measure containing 10 measures of hydrogen.

CHLORAMILAL.—This is the product of the action of dry chlorine on purified potato-oil; when pure, it is an oily, yellowish liquid, insoluble in water, dissolved by alcohol and ether, and having a taste, feeble at first, but which afterwards becomes exceedingly acrid. It boils at 356°. By analysis this substance is found to contain $C_{20}H_{17}Cl_3O_4$.

VALERIANIC ACID.—M. Dumas has shown that when a mixture of equal parts quicklime and hydrate of potash is moistened with alcohol and the whole subjected to gentle heat, out of contact of air, the alcohol is oxidized to acetic acid, with evolution of pure hydrogen gas. At a higher temperature, the acetate of potash produced is in turn decomposed, yielding carbonate of potash and light carburetted hydrogen. Wood-spirit, by similar treatment, yields hydrogen and formiate of potash, which, as the heat increases, becomes converted into oxalate, and eventually into carbonate, with continued disengagement of hydrogen. In like manner potato-oil, the third alcohol, suffers under similar circumstances, conversion into a new acid, bearing to it the same relation that acetic acid does to common alcohol, and formic acid to wood-spirit, hydrogen being at the same time evolved. The body thus produced is found to be identical with a volatile oily acid, distilled from the root of the *valeriana officinalis*.*

In preparing artificial valerianic acid, the potato-oil is heated in a flask with about ten times its weight of the above-mentioned alkaline mixture during the space of 10 or 12 hours; the heat is applied by a bath of oil or fusible metal raised to the temperature of 390° or 400°. When cold, the white, solid residue is removed by breaking the vessel, and quickly immersed into cold water; a slight excess of sulphuric or phosphoric acid is then added, and the whole subjected to distillation. Water and hydrated valerianic acid pass over and are easily separated. When this hydrate is distilled alone, it undergoes decomposition; water first appears, and eventually the pure acid, in the form of a thin, fluid, colorless oil, of the persistent and characteristic odor of valerian-root. It has a sharp and acid taste, reddens litmus strongly, bleaches the tongue, and burns when inflamed with a bright, yet smoky light. Valerianic acid has a density of ·937°; it boils at 347°. Placed in contact with water, it absorbs a certain quantity, and is itself to a certain extent soluble. The salts of this acid presents but little interest, as few among them seem to be susceptible of crystallizing. The liquid acid is found by analysis to contain $C_{10}H_9O_3+HO$, and the silver-salt, $AgO+C_{10}H_9O_3$. The hydrate above referred to, always produced when the acid is liberated from combination in contact with water, contains 3 eq. of water.

If an open-topped jar be set in a plate containing a little water, and having beneath it a capsule with heated platinum-black, upon which potato oil is slowly dropped in such quantity as to be absorbed by the powder, the sides of the jar become speedily moistened with an acid liquid, which collects in the plate, and may be easily examined. This liquid, saturated with baryta-water, evaporated to dryness, and the product distilled with solution of phosphoric acid, yields valerianic acid.

CHLOROVALERISIC ACID.—When dry chlorine is passed for a long time into pure valerianic acid, in the dark, the gas is absorbed in great quantity, and much hydrochloric acid produced; towards the end of the operation, a little heat becomes necessary. The product is a semi-fluid, transparent substance, heavier than water, odorous, and of acrid, burning taste. It does not congeal when exposed to a very low temperature, but acquires complete fluidity when heated to 86°. It cannot be distilled without decomposition. When put into water, it forms a thin, fluid hydrate, which afterwards dissolves to a

* Ann. Chim. et Phys., lxxiii. p. 113.

considerable extent. This body is freely soluble in alkalies, from which it is again precipitated by the addition of an acid. Chlorovalerisic acid contains $C_{10}H_6Cl_3O_3+HO$.

CHLOROVALEROSIC ACID.—This is the ultimate product of the action of chlorine on the preceding substance, aided by exposure to the sun. It resembles chlorovalerisic acid in appearance and properties, being semi-fluid and colorless, destitute of odor, of powerful pungent taste, and heavier than water. It can neither be solidified by cold, nor distilled without decomposition. In contact with water, it forms a hydrate containing 3 eq. of that substance, which is slightly soluble. In alcohol and ether it dissolves with facility. It forms salts with bases, of which the best defined is that of silver. Chlorovalerosic acid is composed of $C_{10}H_5Cl_4O_3+HO$.

FUSEL-OIL FROM GRAIN.—This substance, which is sometimes produced in very large quantity, being probably like the potato-oil, generated during fermentations, is stated by Mulder to be a mixture of "oil of corn" with œnanthic ether, œnanthic acid, and occasionally margaric acid. The origin of this latter substance is by no means clear; it may possibly be produced by an alteration of the œnanthic acid. At the same time it should be remembered that distillers are sometimes in the habit of introducing a little soap or fat of some kind into the still to equalize the boiling and break the bubbles; the presence of the margaric acid may thus be accidental. The corn-oil has a very powerful odor, resembling that of some of the umbelliferous plants; it is unaffected by solution of caustic potash, and contains $C_{24}H_{17}O$.*

The substances discussed in the three next sections have but little relation to the alcohols; they may, however, be here most conveniently described.

BITTER-ALMOND OIL, AND ITS PRODUCTS.

The volatile oil of bitter almonds possesses a very high degree of interest, from its study having, in the hands of MM. Liebig and Wöhler,† led to the first discovery of a compound organic body capable of entering into direct combination with elementary principles, as hydrogen, chlorine, and oxygen, and playing in some degree the part of a metal. The oil is supposed to be the hydruret of a salt-basyle, containing $C_{14}H_5O_2$, called *benzoyle*, from its relation to benzoic acid, which radical is to be traced throughout the whole series; it has not yet been isolated.

Table of Benzoyle-compounds.

Benzoyle, symbol Bz	$C_{14}H_5O_2$
Hydruret of benzoyle; bitter-almond oil	$C_{14}H_5O_2+H$
Oxide of benzoyle; benzoic acid	$C_{14}H_5O_2+O$
Chloride of benzoyle	$C_{14}H_5O_2+Cl$
Bromide of benzoyle	$C_{14}H_5O_2+Br$
Iodide of benzoyle	$C_{14}H_5O_2+I$
Sulphuret of benzoyle	$C_{14}H_5O_2+S$

HYDRURET OF BENZOYLE; BITTER-ALMOND OIL. BzH.—This substance is prepared in large quantities, principally for the use of the perfumer, by dis-

* Ann. der Chemie und Pharmacie, xxiv. p. 248; xli. p. 53; xlv. p. 67; also Pharmaceutical Journal, ii. p. 601.
† Annalen der Pharmacie, iii. p. 249.

tilling with water the paste of bitter-almonds, from which the fixed oil has been expressed. It certainly does not pre-exist in the almonds: the fat oil obtained from them by pressure is absolutely free from every frace of this principle; it is formed by the action of water upon a peculiar crystallizable substance, hereafter to be described, called *amygdaline*, aided in a very extraordinary manner by the presence of the pulpy albuminous matter of the seed. The crude oil has a yellow color, and contains a very considerable quantity of hydrocyanic acid, whose origin is cotemporaneous with that of the oil itself; it is agitated with dilute solution of protochloride of iron mixed with hydrate of lime in excess, and the whole subjected to distillation; water passes over, accompanied by the now purified essential oil, which is to be left for a short time in contact with a few fragments of fused chloride of calcium to free it from water.

Pure hydruret of benzoyle is a thin, colorless liquid, of great refractive power, and peculiar and very agreeable odor; its density is 1·043, and its boiling-point, 356°; it is soluble in about 30 parts of water, and is miscible in all proportions with alcohol and ether. Exposed to the air, it greedily absorbs oxygen, and becomes converted into a mass of crytallized benzoic acid. Heated with solid hydrate of potash, it disengages hydrogen, and yields benzoate of the base. The vapor of the oil is inflammable, and burns with a bright flame and much smoke. It is very doubtful whether pure bitter-almond oil is poisonous; the crude product, sometimes used for imparting an agreeable flavor to puddings, custards, &c., and even publicly sold for that purpose, is in the highest degree dangerous.

Oxide of benzoyle; benzoic acid. BzO.—This is the sole product of the oxidation at a moderate temperature of bitter-almond oil; it is not, however, thus obtained for the purposes of experiment and of pharmacy. Several of the balsams yield benzoic acid in great abundance, more especially the concrete resinous variety known under the name of *gum-benzoin*. When this substance is exposed to a gentle heat in a subliming vessel, the benzoic acid is volatilized, and may be condensed by a suitable arrangement. The simplest and most efficient apparatus for this and all similar operations, is the contrivance of Dr. Mohr; it consists of a shallow iron pan over the bottom of which the substance to be sublimed is thinly spread; a sheet of bibulous paper, pierced with a number of pin-holes, is then stretched over the vessel, and a cap made of thick, strong drawing or cartridge-paper, secured by a string or hoop over the whole. The pan is placed upon a sand-bath and slowly heated to the requisite temperature; the vapor of the acid condenses in the cap, and the crystals are kept by the thin paper diaphragm from falling back again into the pan. Benzoic acid thus obtained assumes the form of light, feathery, colorless crystals, which exhale a fragrant odor, not belonging to the acid itself, but due to a small quantity of a volatile oil. A more productive method of preparing the acid is to mix the powdered gum-benzoin very intimately with an equal weight of hydrate of lime, to boil this mixture with water, and to decompose the filtered solution, concentrated by evaporation to a small bulk, with excess of hydrochloric acid; the benzoic acid crystallizes out on cooling in thin plates, which may be drained upon a cloth filter, pressed, and dried in the air. By sublimation, which is then effected with trifling loss, the acid is obtained perfectly white.

Fig. 162.

Benzoic acid is inodorous when cold, but acquires a faint smell when gently warmed; it melts just below 248°, and sublimes at a temperature a little above;

it boils at 462°, and emits a vapor of the density of 4·27. It dissolves in about 200 parts of cold, and 25 parts of boiling water, and with great facility in alcohol. Benzoic acid is neither affected by boiling concentrated nitric acid, nor by chlorine. The crystals obtained by sublimation, or by the cooling of a hot aqueous solution, contain an equivalent of water, which is basic, or $C_{14}H_5O_3+HO$.

All the benzoates have a greater or less degree of solubility; they are easily formed, either directly, or by double decomposition. *Benzoates of the alkalis* and of *ammonia* are very soluble, and somewhat difficult to crystallize. *Benzoate of lime* forms groups of small colorless needles, which require 20 parts of cold water for solution. The salts of *baryta* and *strontia* are soluble with difficulty in the cold. Neutral *benzoate of the peroxide of iron* is a soluble compound, but the basic salt obtained by neutralizing as nearly as possible by ammonia a solution of peroxide of iron, and then adding benzoate of ammonia, is quite insoluble. Peroxide of iron is sometimes thus separated from other metals in practical analysis. *Benzoate* and *sub-benzoate of lead* are feebly soluble in the cold. *Benzoate of silver* crystallizes in thin transparent plates, which blacken on exposure to light.

SULPHOBENZOIC ACID.—Benzoic acid is soluble without change in concentrated oil of vitriol, and is precipitated by the addition of water; it combines, however, with anhydrous sulphuric acid, generating a compound acid analogous to the sulphovinic, but bibasic, forming a neutral and an acid series of salts. The barytic compound is easily prepared by dissolving in water the viscid mass produced by the union of the two bodies, and saturating the solution with carbonate of baryta. On adding hydrochloric acid to the filtered liquid, and allowing the whole to cool, acid sulphobenzoate of baryta crystallizes out. This salt has an acid reaction, and requires 20 parts of cold water for solution; the neutral salt is much more soluble. The hydrated acid is easily obtained by decomposing the sulphobenzoate of baryta by dilute sulphuric acid; it forms a white, crystalline, deliquescent mass, very stable and permanent, which probably contains $C_{14}H_5O_3, SO_3+2HO$.*

When dry benzoate of lime is distilled at a high temperature, it yields *benzone*, which, when pure, is a thick, oily colorless liquid, of peculiar odor; it boils at 482°, or a little above, and contains $C_{13}H_5O$; carbonate of lime remains in the retort; the reaction is thus perfectly analogous to that by which acetone is produced by the distillation of a dry acetate.

$$CaO\,,\,C_{14}H_5O_{13}=C_{13}H_5O \text{ and } CaO\,,\,CO_2.$$

The benzone is, however, always accompanied by secondary products, due to the irregular and excessive temperature, as naphthaline, carbonic oxide, and *benzine*, a body next to be described.‡

If crystallized benzoic acid be mixed with three times its weight of hydrate of lime, and the whole distilled at a temperature slowly raised to redness, in a coated glass or earthen retort, water, and a volatile oily liquid, termed *benzine*, pass over, while carbonate of lime, mixed with excess of hydrate of lime, remains in the retort. The benzine separated from the water and rectified, forms a thin, limpid, colorless liquid, of strong but not very disagreeable odor, insoluble in water, but miscible with alcohol, having a density of ·850, and boiling at 187° F.; the sp. gr. of its vapor is 2·738. Cooled to 32°, it solidifies to a white, crystalline mass. Benzine contains carbon and hydrogen only, in the proportion of 2 eq. of the former to 1 of the latter, or

* Mitscherlich, Lehrbuch, i. p. 108.
† Péligot. Ann. Chim. et Phys., lvi. p. 59.

probably $C_{12}H_6$. It is produced by the resolution of the benzoic acid into benzine and carbonic acid, the water taking part in the reaction.

$$C_{14}H_6O_4 = C_{12}H_6 \text{ and } C_2O_4.$$

Benzine is identical with the bicarburet of hydrogen, several years ago discovered by Mr. Faraday in the curious liquid condensed during the compression of oil-gas, of which it forms the great bulk, being associated with an excessively volatile hydrocarbon, containing carbon and hydrogen in the ratio of the equivalents, the vapor of which required for condensation a temperature of 0°. It received the name *etherine*, from its supposed connection with alcohol and ether.

SULPHOBENZIDE AND HYPOSULPHOBENZIC ACID.—Benzine combines directly with anhydrous sulphuric acid, to a thick viscid liquid, soluble in a small quantity of water, but decomposed by a larger portion, with separation of a crystalline matter, the *sulphobenzide*, which may be washed with water, in which it is nearly insoluble, dissolved in ether, and left to crystallize by spontaneous evaporation. It is a colorless, transparent substance, of great permanence, fusible at 212°, bearing distillation without change, and resisting the action of acids and other energetic chemical agents. Sulphobenzide contains $C_{12}H_5SO_2$. The acid liquid from which the preceding substance has been separated, neutralized by carbonate of baryta and filtered, yields *hyposulphobenzate of baryta*, which is a soluble salt, but crystallizes in an imperfect manner. By double decomposition with sulphate of copper, a compound of the oxide of that metal is obtained, which forms fine, large, regular crystals. The hydrate of hyposulphobenzic acid is prepared by decomposing the copper-salt with sulphuretted hydrogen; a sour liquid is obtained, which furnishes, by evaporation, a crystalline residue, containing $C_{12}H_5S_2O_5+HO$. The salts of *potash*, *soda*, *ammonia*, and of the oxides of *zinc*, *iron*, *silver*, crystallize freely. This compound acid can be prepared by dissolving benzine in Nordhausen sulphuric acid.

NITROBENZIDE.—Ordinary nitric acid, even at a boiling temperature, has no action on benzine; the red fuming acid attacks it, with the aid of heat, with great violence. The product, on dilution, throws down a heavy, oily, yellowish, and intensely sweet liquid, which has an odor resembling that of bitter-almond oil. Its density is 1·209; it boils at 415°, and distils unchanged. It is but little affected by acids, alkalis, or chlorine, and is quite insoluble in water. Nitrobenzide contains $C_{12}H_5NO_4$. When nitrobenzide is heated with an alcoholic solution of caustic potash, and the product subjected to distillation, a red compound passes over, which separates, on cooling, in large red crystals, which are nearly insoluble in water, but dissolve with facility in ether and alcohol. This substance, which is called *azobenzide*, melts at 149°, and boils at 379°; it contains $C_{12}H_5N$.*

Benzine and chlorine combine when exposed to the rays of the sun; the product is a solid, crystalline, fusible substance, insoluble in water, containing $C_{12}H_6Cl_6$, called *chlorbenzine*. When this substance is distilled, it is decomposed into hydrochloric acid, and a volatile liquid, *chlorbenzide*, composed of $C_{12}H_3Cl_3$.

CHLORIDE OF BENZOYLE. BzCl.—This compound is prepared by passing dry chlorine gas through pure bitter almond oil, as long as hydrochloric acid continues to be formed; the excess of chlorine is then expelled by heat. Chloride of benzoyle is a colorless liquid, of peculiar, disagreeable, and pungent odor. Its density is 1·106. The vapor is inflammable, and burns with a tint of green. It is decomposed slowly by cold, and quickly by boiling

* Mitscherlich, Lehrbuch, i. p. 100.

water, into benzoic and hydrochloric acids; with an alkaline hydrate, benzoate of the base, and chloride of the metal, are generated. If, in the preparation of chloride of benzoyle, the chlorine contain vapor of water, a peculiar crystalline substance is produced, containing $C_{42}H_{18}O_8$, which seems to be a compound of hydrated benzoic acid and bitter-almond oil.

When pure chloride of benzoyle and dry ammoniacal gas are presented to each other, the ammonia is energetically absorbed, and a white, solid substance produced, which is a mixture of sal-ammoniac and a highly interesting body, *benzamide*. The sal-ammoniac is removed by washing with cold water, and the benzamide dissolved in boiling water, and left to crystallize. It forms colorless, transparent, prismatic, or platy crystals, fusible at 239°, and volatilizable at a higher temperature. It is but slightly soluble in cold, freely in boiling water, also in alcohol and ether. Benzamide corresponds to oxamide, both in composition and properties; it contains $C_{14}H_7NO_2$, or benzoate of oxide of ammonium *minus* 2 eq. of water, and it suffers decomposition by both acid and alkaline solutions, yielding, in the first case, a salt of ammonia and benzoic acid, and in the second, free ammonia and a benzoate.

Iodide of benzoyle. BzI.—This is prepared by distilling the chloride of benzoyle with iodide of potassium; it forms a colorless, crystalline, fusible mass, decomposed by water and alkalis, in the same manner as the chloride. The *bromide* of benzoyle, BzBr, has very similar properties. The *sulphuret*, BzS, is a yellow oil, of offensive smell, which solidifies, at a low temperature, to a soft, crystalline mass. *Cyanide* of benzoyle, Bz, C_2N, obtained by heating the chloride with cyanide of mercury, forms a colorless, oily, inflammable, liquid, of pungent odor, somewhat resembling that of cinnamon. All these compounds yield benzamide with dry ammonia.

Mandelic acid.—Crude bitter-almond oil is dissolved in water, mixed with hydrochloric acid, and evaporated to dryness; the residue is boiled with ether, which dissolves out the new substance, and leaves sal-ammoniac. Mandelic acid forms small, indistinct, white crystals, which fuse, and afterwards suffer decomposition by heat, evolving an odor resembling that of the flowers of the hawthorn, and leaving a bulky residue of charcoal. It is freely soluble in water, alcohol, and ether, has a strong acid taste and reaction, and forms a series of crystallizable salts, with metallic oxides. This substance contains $C_{16}H_7O_5+HO$, or the elements of bitter-almond oil, and formic acid; it owes its origin to the peculiar action of strong mineral acids on the hydrocyanic acid of the crude oil, by which that body suffers resolution into formic acid and ammonia. It is decomposed by oxidizing bodies, as peroxide of manganese, nitric acid, and chlorine, into bitter-almond oil and carbonic acid.

Hydrobenzamide.—Pure bitter-almond oil is digested for some hours at about 120°, with a large quantity of strong solution of ammonia; the resulting white crystalline product is washed with cold ether, and dissolved in alcohol; the solution, left to evaporate spontaneously, deposits the *hydrobenzamide* in regular, colorless crystals, which have neither taste nor smell. This substance melts at a little above 212°, is readily decomposed by heat, dissolves with ease in alcohol, but is insoluble in water; the alcoholic solution is resolved by boiling into ammonia and bitter-almond oil; a similar change happens with hydrochloric acid. Hydrobenzamide contains $C_{42}H_{18}N_2$, or the elements of three equivalents of bitter-almond oil, and 2 of ammonia, *minus* 6 equivalents of water.

When impure bitter-almond oil is employed in this experiment, the products are different, three other compounds being obtained, called by M. Laurent *benzhydramide*, *azobenzoyle*, and *nitrobenzoyle*. The first is isomeric with hydrobenzamide, but differs in properties.

Benzoine.—This substance is found in the residue contained in the retort

from which bitter-almond oil has been distilled with lime and oxide of iron, to free it from hydrocyanic acid; it is a product of the action of alkalis and alkaline earths on the crude oil, and is said to be only generated in the presence of that remarkable acid. It is easily extracted from the pasty mass by dissolving out the lime and oxide of iron by hydrochloric acid, and boiling the residue in alcohol. Benzoine forms colorless, transparent, brilliant, prismatic crystals, tasteless and inodorous; it melts at 248°, and distils without decomposition. Water, even at a boiling heat, dissolves but a small quantity of this body; boiling alcohol takes it up in larger proportion; it dissolves in cold oil of vitriol, with violet color. The vapor, transmitted through a red-hot tube, yields an oily liquid, changeable by exposure to air to benzoic acid, and which is, probably, bitter-almond oil. Benzoine contains $C_{14}H_6O_2$, and is, consequently, an isomeric modification of bitter-almond oil.

Benzile.—This curious compound is a product of the action of chlorine on benzoine; the gas is conducted into the fused benzoine as long as hydrochloric acid continues to be formed, and the crystalline residue purified by solution in alcohol. It forms large, transparent, sulphur-yellow crystals, fusible at 200°, unaltered by distillation, and quite insoluble in water. It dissolves freely in alcohol, ether, and concentrated sulphuric acid, from which it is precipitated by water. Benzile is composed of $C_{14}H_5O_2$, and is therefore *isomeric with the radical of the benzoyle series.**

Benzilic acid.—Benzoine and benzile dissolve with violet-tint in alcoholic solution of caustic potash: by long boiling the liquid becomes colorless and is then found to contain a salt of a peculiar acid, called the *benzilic*, which is easily obtained by adding hydrochloric acid to the filtered liquid, and leaving the whole to cool. Benzilic acid forms small, colorless, transparent crystals, slightly soluble in cold, more readily in boiling water; it melts at 248°, and cannot be distilled without decomposition. It dissolves in cold concentrated sulphuric acid with a fine carmine-red color. Benzilic acid contains $C_{28}H_{11}O_5$ $+HO$, or 2 eq. of benzile and 1 eq. water.

Benzimide.—This is a white, inodorous, shining, crystalline substance, occasionally found in crude bitter-almond oil. It is insoluble in water, and but slightly dissolved by boiling alcohol and ether. Oil of vitriol dissolves it with dark indigo-blue color, becoming green by the addition of a little water. This reaction is characteristic. Benzimide contains $C_{28}H_{11}NO_4$.

Hippuric acid.—This interesting substance is in some measure related to the benzoyle-compounds. It occurs, often in large quantity, in combination with potash or soda, in the urine of horses, cows, and other graminivorous animals. It is best prepared by evaporating in a water-bath perfectly fresh cow-urine to about a tenth of its volume, filtering from the deposit, and then mixing the liquid with excess of hydrochloric acid. The brown crystalline mass which separates on cooling is dissolved in boiling water, and treated with a stream of chlorine gas until the liquid assumes a light amber color, and begins to exhale the odor of that substance; it is then filtered, and left to cool. The still impure acid is re-dissolved in water, neutralized with carbonate of soda, and boiled for a short time with animal charcoal; the hot filtered solution is, lastly, decomposed by hydrochloric acid.

Hippuric acid in a pure state crystallizes in long, slender, milk-white, and exceedingly frangible square prisms, which have a slight bitter taste, fused on the application of heat, and require for solution about 400 parts of cold water; it also dissolves in hot alcohol. It has an acid reaction, and forms salts with bases, many of which are crystallizable. Exposed to a high temperature, hippuric acid undergoes decomposition, yielding benzoic acid, benzoate of am-

* Laurent, Ann. Chim. et Phys., lix. p. 397; also Liebig, in Geiger's Pharmacie, i. p. 680.

monia, and a fragrant oily matter, and a coaly residue. With hot oil of vitriol, it gives off benzoic acid. Hippuric acid contains $C_{18}H_8NO_5+HO$.*

If, in the preparation of this substance, the urine be in the slightest degree putrid, the hippuric acid is all destroyed during the evaporation, ammonia is disengaged in large quantity, and the liquid is then found to yield nothing but benzoic acid, not a trace of which can be discovered in the unaltered secretion. Complete putrefaction effects the same change; benzoic acid might be thus procured to almost any extent.

When benzoic acid is taken internally, it is rejected from the system in the state of hippuric acid, which is then found in the urine.

SALICYLE, AND ITS COMPOUNDS.

SALICINE.—The leaves and young bark of the poplar, willow, and several other trees, contain a peculiar crystallizable, bitter principle, called *salicine*, which in some respects resembles the vegeto-alkalis cinchonia and quina, having febrifuge properties. It differs essentially, however, from these bodies in being destitute of nitrogen, and in not forming salts with acids. Salicine may be prepared by exhausting the bark with boiling water, concentrating the solution to a small bulk, digesting the liquid with powdered oxide of lead, and then, after freeing the solution from lead by a stream of sulphuretted hydrogen gas, evaporating until the salicine crystallizes out on cooling. It is purified by treatment with animal charcoal, and re-crystallization.

Salicine forms small white, silky needles, of intensely bitter taste, which have no alkaline reaction. It melts and decomposes by heat, burning with bright flame, and leaving a residue of charcoal. It is soluble in 5-6 parts of cold water, and in a much smaller quantity when boiling hot. Oil of vitriol colors it deep red. This substance is found on analysis to contain $C_{21}H_{14}O_{11}$.

When salicine is distilled with a mixture of bichromate of potash and sulphuric acid, it yields, among other products, a yellow, sweet-scented oil, *which is found to be identical with the volatile oil distilled from the flowers of the spiræa ulmaria, or common meadow-sweet.* This substance appears to be the hydruret of a compound salt-radical, *salicyle*, containing $C_{14}H_5O_4$; it has the properties of a hydrogen-acid.†

Table of Salicyle-compounds.

Salicyle (symb. Sl)	$C_{14}H_5O_4$
Hydrosalicylic acid	$C_{14}H_5O_4+H$
Salicyluret of potassium	$C_{14}H_5O_4+K$
Iodide of salicyle	$C_{14}H_5O_4+I$
Bromide of salicyle	$C_{14}H_5O_4+Br$
Salicylic acid	$C_{14}H_5O_4+O$

HYDROSALICYLIC ACID; ARTIFICIAL OIL OF MEADOW-SWEET. SlH.—One part of salicine is dissolved in 10 of water, and mixed in a retort with 2½ parts of oil of vitriol diluted with 10 parts of water; gentle heat is applied, and, after the cessation of the effervescence first produced, the mixture is distilled. The yellow oily product is separated from the water, and purified by rectification from chloride of calcium. It is thin, colorless, and transparent,

* M. Dessaignes has observed that, under the influence of the strong acids, hippuric acid is converted into benzoic acid, which is set free, and sugar of gelatin which unites the acid employed. This decomposition may be thus represented:

$$C_{18}H_8NO_5+2\dot{H}O=C_{14}H_5O_3+C_4H_5NO_4. \qquad \text{R. B.}$$

† Piria, Ann. Chim. et Phys., lxix. p. 281.

but acquires a red tint by exposure to the air. Water dissolves a sensible quantity of this substance, acquiring the odor of the oil, and the characteristic property of striking a deep violet color with a salt of peroxide of iron. Alcohol and ether dissolve it in all proportions. It has a density of 1·173, and boils at 385°, when heated alone. Hydrosalicylic acid decomposes the alkaline carbonates even in the cold; it is acted upon with great energy by chlorine and bromine. By analysis it is found to contain $C_{14}H_6O_4$, or the same elements as crystallized benzoic acid, and the density of its vapor is also the same, being 4·276.

Salicyluret of potassium. KSl.—This compound is easily prepared by mixing the oil with a strong solution of caustic potash; it separates, on agitation, as a yellow crystalline mass, which may be pressed between folds of blotting-paper, and re-crystallized from alcohol. It forms large, square, golden-yellow tables, which have a greasy feel, and dissolve very easily both in water and alcohol; the solution has an alkaline reaction. When quite dry, the crystals are permanent in the air; but in a humid state they soon become greenish and eventually change to a black, soot-like substance, insoluble in water, but dissolved by spirit and by solution of alkali, called *melanic acid.* Acetate of potash is formed at the same time. Melanic acid contains $C_{10}H_4O_5$. The crystals of salicyluret of potassium contain water, which cannot be expelled without partial decomposition of the salt.

Salicyluret of ammonium, NH_4,Sl, crystallizes in yellow needles, which are quickly destroyed with production of ammonia and the hydruret. *Salicyluret of barium*, Ba,$C_{14}H_5O_4$+2HO, forms fine yellow acicular crystals, which are but slightly soluble in the cold. *Salicyluret of copper* is a green insoluble powder, containing Cu,$C_{14}H_5O_4$.

Salicylic acid. SlO.—The oxygen compound is obtained by heating hydruret of salicyle with excess of solid hydrate of potash; the mixture is at first brown, but afterwards becomes colorless; hydrogen gas is disengaged during the reaction. On dissolving the melted mass in water, and adding a slight excess of hydrochloric acid, the salicylic acid separates in crystals, which are purified by re-solution in hot water. This substance very much resembles benzoic acid; it is very feebly soluble in cold water, is dissolved in large quantities by alcohol and ether, and may be sublimed with the utmost ease. It is charred and decomposed by hot oil of vitriol, and attacked with great violence by strong heated nitric acid. Salicylic acid contains $C_{14}H_5O_5H$+HO.

Chloride of salicyle. SlCl.—Chlorine acts very strongly upon the hydruret of salicyle; the liquid becomes heated and disengages large quantities of hydrochloric acid. The product is a slightly yellowish crystalline mass, which, when dissolved in hot alcohol, yields colorless tabular crystals of pure chloride, having a pearly lustre. Chloride of salicyle is insoluble in water; it dissolves freely in alcohol, ether, and solutions of the fixed alkalis; from the latter it is precipitated unaltered by the addition of an acid, differing much in this respect from chloride of benzoyle. It is not even decomposed by long ebullition with a concentrated solution of caustic potash. Heated in a retort, it melts and volatilizes, condensing in the cool part of the vessel in long, snow-white needles. The odor of this substance is peculiar and by no means agreeable, and its taste is hot and pungent.

Chloride of salicyle combines directly with metallic oxides; with potash it forms small red crystalline scales, very soluble in water. The corresponding compound of baryta, prepared from the foregoing by double decomposition, is an insoluble, crystalline, yellow powder, containing $C_{14}H_5O_4Cl$+BaO.

Bromide of salicyle.—SlBr.—The bromide is prepared by the direct action of bromide on the hydruret of salicyle; it crystallizes in small colorless

needles, and very closely resembles in properties the chloride. The hydruret of salicyle dissolves a large quantity of iodine, acquiring thereby a brown colour, but forming no combination; the iodide may, however, be procured, by distilling iodide of potassium with chloride of salicyle. It sublimes as a blackish-brown fusible mass.

CHLOROSAMIDE.—The action of dry ammoniacal gas on pure chloride of salicyle is very remarkable; the gas is absorbed in large quantity, and a solid yellow, resinous-looking compound produced, which dissolves in boiling ether, and separates as the solution cools in fine yellow iridescent crystals; this, and a little water are the only products, not a trace of sal-ammoniac can be detected. Chlorosamide is nearly insoluble in water; it dissolves without change in ether, and in absolute alcohol; with hot rectified spirit it is partially decomposed, with disengagement of ammonia. Boiled with an acid, it yields an ammoniacal salt of the acid, and chloride of salicyle; with an alkali, on the other hand, it gives free ammonia, while chloride of salicyle remains dissolved. Chlorosamide contains $C_{42}H_{15}N_2O_6Cl_3$; it is formed by the addition of 2 eq. of ammonia to 3 eq. of chloride of salicyle, and the subsequent separation of 6 eq. of water. A corresponding and very similar substance, *bromosamide*, is formed by the action of ammonia on the bromide of salicyle.

PHLORIDZINE.—This is a substance bearing a great likeness to salicine, found in the root-rind of the apple and cherry-tree, and extracted by boiling alcohol. It forms fine, colorless, silky needles, soluble in 1,000 parts of cold water, but freely dissolved by that liquid when hot; it is also soluble without difficulty in alcohol. It contains $C_{21}H_{15}O_{12}$.

CINNAMYLE, AND ITS COMPOUNDS.

The essential oil of cinnamon seems to possess a constitution analogous to that of bitter-almond oil; it passes by oxidation into a volatile acid, the *cinnamic*, which resembles in the closest manner benzoic acid. The supposed radical bears the name of *cinnamyle;* it has not been isolated.

Table of Cinnamyle-compounds.

Cinnamyle, symbol Ci	$C_{18}H_7O_2$
Hydruret of cinnamyle; oil of cinnamon ..	$C_{18}H_7O_2+H$
Oxide of cinnamyle; cinnamic acid . .	$C_{18}H_7O_2+O$
Chloride of cinnamyle	$C_{18}H_7O_2+Cl$

HYDRURET OF CINNAMYLE; OIL OF CINNAMON. CiH.—Cinnamon of excellent quality is crushed, infused twelve hours in a saturated solution of common salt, and then the whole subjected to rapid distillation. Water passes over, milky from essential oil, which after a time separates. It is collected and left for a short time in contact with chloride of calcium. This fragrant and costly substance has, like most of the volatile oils, a certain degree of solubility in water; it is heavier than that liquid, and sinks to the bottom of the receiver in which the distilled products have been collected. It contains, according to M. Dumas, $C_{18}H_8O_2$.

CINNAMIC ACID. CiO.—When pure oil of cinnamon is exposed to the air, or enclosed in a jar of oxygen, it is quickly converted by absorption of the gas into a mass of white crystalline matter, which is hydrated cinnamic acid; this is the only product. Cinnamic acid is found in Peruvian and Tolu balsams, associated with benzoic acid, and certain oily and resinous substances; it may be procured by the following process in great abundance, and in a state of perfect purity. Old, hard Tolu balsam is reduced to powder and intimately mixed with an equal weight of hydrate of lime; this mixture is

boiled for some time in a large quantity of water, and filtered hot. On cooling, cinnamate of lime crystallizes out, while benzoate of lime remains in solution. The impure salt is redissolved in boiling water, digested with animal charcoal, and, after filtration, suffered to crystallize. The crystals are drained and pressed, once more dissolved in hot water, and an excess of hydrochloric acid being added, the whole is allowed to cool; the pure cinnamic acid separates in small plates or needle-formed crystals of perfect whiteness. From the original mother-liquor much benzoic acid can be procured.

The crystals of cinnamic acid are smaller and less distinct than those of benzoic acid, which in most respects it very closely resembles. It melts at 248°, and enters into ebullition and distils without change at 560°; the vapor is pungent and irritating. Cinnamic acid is much less soluble, both in hot and cold water, than benzoic; a hot saturated solution becomes on cooling a soft-solid mass of small nacreous crystals. It dissolves with perfect ease in alcohol. Boiling nitric acid decomposes cinnamic acid with great energy, and with production of copious red fumes; a small quantity of a volatile oily liquid, having the odor of bitter-almond oil, distils over, and a little benzoic acid remains in the retort in which the experiment is made. When cinnamic acid is heated in a retort with a mixture of strong solution of bichromate of potash and oil of vitriol, it is almost instantly converted into benzoic acid, which afterwards distils over with the vapor of water: the odor of bitter-almond oil is at the same time very perceptible. The action of chlorine is different; no benzoic acid is formed, but other products, which have been as yet imperfectly studied.

Cinnamic acid forms with bases a variety of salts which are very similar to the benzoates. The crystallized acid contains $C_{18}H_7O_3 + HO$.

Chloro-cinnose.—This is the ultimate product of the action of chlorine on oil of cinnamon by the aid of heat. When purified by crystallization from alcohol, it forms brilliant, colorless needles, fusible, and susceptible of volatilization without change. It is not affected by boiling oil of vitriol, and may be distilled without decomposition in a current of ammoniacal gas. Chlorocinnose contains $C_{18}H_4Cl_4O_2$; it is formed by the substitution in the oil of cinnamon of 4 eq. of chlorine for 4 eq. of hydrogen. The true *chloride of cinnamyle*, Ci Cl, seems to be first formed in considerable quantity, and subsequently decomposed by the continued action of the chlorine; it has not been separated in a pure state; it appears as a very thin, fluid oil, convertible into a crystalline mass by strong solution of potash.

When cinnamon-oil is treated with hot nitric acid, it undergoes decomposition, being converted into hydruret of benzoyle and benzoic acid. With a boiling solution of chloride of lime, the same thing happens, a benzoate of the base being generated. If the oil be heated with solution of caustic potash it remains unaffected; with the solid hydrate, however, it disengages pure hydrogen, and forms a potash-salt, which appears to be the cinnamate. When brought into contact with cold concentrated nitric acid, a crystalline, yellowish, scaly compound is obtained, which is decomposed by water with separation of the oil. With ammonia, a solid substance is produced, which also appears to be a direct compound of the two bodies.

Two varieties of oil of cinnamon are met with in commerce of very unequal value, viz., that of China, and that of Ceylon; the former being considered the best; both are, however, evidently impure. The pure oil may be extracted from them by an addition of cold, strong nitric acid: the crystalline matter which forms after the lapse of a few hours, separated and decomposed by water, yields pure hydruret of cinnamyle.*

* MM. Dumas and Péligot, Ann. Chim. et Phys., lvii. p. 305.

There can be no doubt that the cinnamic acid in Tolu and Peru balsams is gradually formed by the oxidation of an oily matter very closely related to the volatile oil of cinnamon. When these balsams are first imported they are nearly fluid, but gradually acquire consistence by keeping. M. Frémy succeeded in separating from these substances, by the aid of an alcoholic solution of potash, an oil, which could not be distilled without partial decomposition, and which, by the action of hydrate of potash, became in great part converted into cinnamic acid. This substance, called by Frémy *cinnameine*, cannot be looked upon as a pure hydruret of cinnamyle, although it probably contains the latter; its composition is very uncertain. Cinnameine, artificially cooled, was sometimes found to deposit a solid crystalline substance, which had exactly the composition of pure oil of cinnamon, $C_{18}H_8O_2$, and was converted by caustic potash into cinnamic acid; it received the name of *metacinnameine*.*

* Frémy, Ann. Chim. et Phys., lxx. p. 196.

SECTION III.

VEGETABLE ACIDS.

The vegetable acids constitute a very natural and important family or group of compounds, many of which enjoy the property of acidity, *i. e.*, acid reaction to litmus paper, and power of forming stable, neutral, and often crystallizable compounds with bases, to an extent comparable with that of the mineral acids. Some of these bodies are very widely diffused through the vegetable kingdom; others are of much more limited occurrence, being found in some few particular plants only, and very frequently in combination with organic alkaline bases. Many of the vegetable acids are polybasic; and it is remarkable that in the new products, or pyro-acids, to which they often give rise under the influence of heat, this character is usually lost.

The particular acids now to be described are for the most part of extensive and general occurrence; mention will be made of some of the rarer ones in connexion with their respective sources.

Table of vegetable acids.

Tartaric acid	$C_8H_4O_{10}+2HO$
Racemic acid	$C_8H_4O_{10}+2HO$
Citric acid	$C_{12}H_5O_{11}+3HO$
Aconitic, or equisetic acid	C_4HO_3+HO
Malic acid	$C_8H_4O_8+2HO$
Fumaric acid	C_4HO_3+HO
Tannic acid	$C_{18}H_5O_9+3HO$
Gallic acid	C_7HO_3+2HO.

Tartaric acid.—This is the acid of grapes, of tamarinds, of the pine-apple, and of several other fruits, in which it occurs in the state of acid potash-salt; tartrate of lime is also occasionally met with. The tartaric acid of commerce is wholly prepared from the *tartar* or *argol*, an impure acid tartrate of potash, deposited from wine, or rather grape-juice, in the act of fermentation. This substance is purified by solution in hot water, the use of a little pipe-clay, and animal charcoal to remove the coloring-matter of the wine, and subsequent crystallization; it then constitutes *cream of tartar*, and serves for the preparation of the acid. The salt is dissolved in boiling water, and powdered chalk added as long as effervescence is excited, or the liquid exhibits an acid reaction; tartrate of lime and neutral tartrate of potash result; the latter is separated from the former, which is insoluble, by filtration. The solution of tartrate of potash is then mixed with excess of chloride of calcium, which throws down all the remaining acid in the form of lime-salt; this is washed, added to the former portion, and then the whole digested with a sufficient quantity of dilute sulphuric acid to withdraw the base and liberate the organic acid. The filtered solution is cautiously evaporated to a sirupy consistence, and placed to crystallize in a warm situation.

Tartaric acid forms colorless, transparent crystals, often of large size, which have the figure of an oblique rhombic prism more or less modified; these are

permanent in the air, and inodorous; they dissolve with great facility in water, both hot and cold, and are also soluble in alcohol. The solution reddens litmus strongly, and has a pure, clean, acid taste. The aqueous solution is gradually spoiled by keeping. Tartaric acid is bibasic; the crystals contain $C_8H_4O_{10}+2HO$. This substance is consumed in large quantities by the calico-printer, being employed to evolve chlorine from solution of bleaching-powder in the production of white or *discharged* patterns upon a colored ground.

TARTRATES OF POTASH. NEUTRAL TARTRATE; SOLUBLE TARTAR. $2KO,C_8H_4O_{10}$.—The neutral salt may be procured by neutralizing cream of tartar with chalk, as in the preparation of the acid, or by adding carbonate of potash to cream of tartar to saturation; it is very soluble, and crystallizes with difficulty in right rhombic prisms, which are permanent in the air and have a bitter, saline taste.

ACID TARTRATE OF POTASH; CREAM OF TARTAR. $KO,HO,C_8H_4O_{10}$.—The origin and mode of preparation of this substance have been already described. It forms small transparent or translucent prismatic crystals, irregularly grouped together, which grit between the teeth. It dissolves pretty freely in boiling water, but the greater part separates as the solution cools, leaving about $\frac{1}{184}$th or less, dissolved in the cold liquid. The salt has an acid reaction, and a sour taste. When exposed to heat in a close vessel, it is decomposed with evolution of inflammable gas, leaving a mixture of finely-divided charcoal and pure carbonate of potash, from which the latter may be extracted by water. Cream of tartar is almost always produced when tartaric acid in excess is added to a moderately strong solution of a potash-salt, and the whole agitated.

TARTRATES OF SODA.—Two compounds of tartaric acid with soda are known; a *neutral salt*, $2NaO,C_8H_4O_{10}+4HO$, and an *acid salt*, $NaO,HO,C_8H_4O_{10}+2HO$. Both are easily soluble in water, and crystallize. Tartaric acid and bicarbonate of soda form the ordinary *effervescing draughts*.

TARTRATE OF POTASH AND SODA; ROCHELLE OR SEIGNETTE SALT. $KO,NaO,C_8H_4O_{10}+10HO$.—This beautiful salt is made by neutralizing with carbonate of soda a hot solution of cream of tartar, and evaporating to the consistence of thin sirup. It separates in large, transparent, prismatic crystals, the faces of which are unequally developed; these effloresce slightly in the air, and dissolve in 1½ parts of cold water. Acids precipitate cream of tartar from the solution. Rochelle salt has a mild saline taste, and is used as a purgative.

TARTRATES OF AMMONIA.—The *neutral* tartrate is a soluble and efflorescent salt, containing $2NH_4O,C_8H_4O_{10}+2HO$. The *acid* tartrate, $NH_4O,HO,C_8H_4O_{10}$, closely resembles ordinary cream of tartar. A salt corresponding to Rochelle salt also exists, having oxide of ammonium in place of soda.

The tartrates of *lime*, *baryta*, *strontia*, *magnesia*, and of the oxides of most of the metals proper, are insoluble, or nearly so, in water.

[TARTRATE OF POTASH AND PEROXIDE OF IRON. $Fe_2O_3,KO,C_8H_4O_{10}$.—This is obtained by dissolving hydrated peroxide of iron in a boiling solution of cream of tartar. It does not crystallize, but exists as a dark-colored mass, or in garnet-red translucent scales, of a sweetish astringent taste, soluble in 4 parts of water, scarcely soluble in alcohol. The iron exists in this compound in such a condition, that it is not precipitated by potash, soda, ammonia in the cold, or by ferrocyanide of potassium, unless an acid be previously added. It is decomposed by heat of 260°, and at a red heat, the iron is revived.—R. B.]

TARTRATE OF ANTIMONY AND POTASH, OR TARTAR EMETIC.—This is easily made by boiling oxide of antimony in solution of cream of tartar; it is deposited from a hot and concentrated solution in crystals derived from an octahedron with rhombic base, which dissolve without decomposition in 15 parts of

cold, and in 3 of boiling water, and have an acrid and extremely disagreeable metallic taste. The solution is incompatible with, and decomposed by, both acids and alkalis; the former throw down a mixture of cream of tartar and oxide of antimony, and the latter, the oxide, which is again dissolved by great excess of the reagent. Sulphuretted hydrogen separates all the antimony in the state of sulphuret. Heated in a dry state on charcoal before the blowpipe, it yields a globule of metallic antimony. The crystals contain KO,SbO_3 $C_8H_4O_{10}+2HO$.

A solution of tartaric acid dissolves hydrated peroxide of iron in large quantity, forming a brown liquid which has an acid reaction, and dries up by gentle heat to a brown, transparent, glassy substance, destitute of all traces of crystallization. It is very soluble in water, and the solution is not precipitated by alkalis, fixed or volatile. Indeed, tartaric acid added in sufficient quantity to a solution of peroxide salt of iron or alumina, entirely prevents the precipitation of the bases by excess of ammonia. Tartrate and ammoniacal tartrate of iron are used in medicine, these compounds having a less disagreeable taste than most of the iron preparations.

Solution of tartaric acid gives white precipitates with lime and baryta-water and with acetate of lead, which dissolve in excess of the acid; with neutral salts of lime and baryta no change is produced. The effect on solutions of potash-salts has been already noticed.

Action of heat on tartaric acid.—When crystallized tartaric acid is exposed to a temperature of 400° or thereabouts, it melts, loses water, and passes through three different modifications, called in succession *tartralic*, *tartrelic*, and *anhydrous tartaric acid*. The first two are soluble in water, and form salts which have properties completely different from those of ordinary tartaric acid. The third substance, or anhydrous acid, is a white insoluble powder. All three, in contact with water, slowly pass into common tartaric acid. Their composition is thus expressed:—

Ordinary tartaric acid	$C_8H_4O_{10}+2HO$
Tartralic acid	$2C_8H_4O_{10}+3HO$
Tartrelic acid	$C_8H_4O_{10}+HO$
Anhydrous tartaric acid	$C_8H_4O_{10}$

The analogy borne by these bodies to the several modifications of phosphoric acid will be at once evident.*

Pyrotartaric acid.—When crystallized tartaric acid is subjected to destructive distillation, a heavy acid liquid containing this substance passes over, accompanied by a large quantity of carbonic acid; in the retort is left a semifluid black mass, which, by further heating, gives combustible gases, an empyreumatic oil, and a residue of charcoal. The distilled product exhales a powerful odor of acetic acid, and is with great difficulty purified. Pyrotartaric acid forms a series of salts, and an ether; it is supposed to contain $C_6H_3O_5+HO$. A second pyro-acid sometimes separates in crystals from the preceding compound, and may be obtained in larger quantity by the distructive distillation of cream of tartar; it is composed of $C_5H_3O_3+HO$.

Racemic acid; paratartaric acid.—The grapes cultivated in certain districts of the Upper Rhine, and also in the Vosges, in France, contain, in association with tartaric acid, another and peculiar acid body, to which the

* Frémy, Ann. Chim. et Phys., lxviii. p. 353.

term *racemic acid* is given; it is rather less soluble than tartaric acid, and separates first from the solution of that substance. Between these two acids, however, the greatest possible resemblance exists; they have exactly the same composition, and yield, when exposed to heat, the same products; the salts of racemic acid correspond also, in the closest manner, with the tartrates. A solution of this acid precipitates a neutral salt of lime, which is not the case with tartaric acid.

CITRIC ACID.—Citric acid is obtained in large quantity from the juice of limes and lemons; it is found in many other fruits, as in gooseberries, currants, &c., in conjunction with another acid, the malic. In the preparation of this acid, the juice is allowed to ferment a short time, in order that mucilage, and other impurities may separate and subside; the clear liquor is then carefully saturated with chalk, which forms, with the citric acid, an insoluble compound. This is thoroughly washed, decomposed by the proper quantity of sulphuric acid, diluted with water, and the filtered solution evaporated to a small bulk, and left to crystallize. The product is drained from the mother-liquor, redissolved, digested with animal charcoal, and again concentrated to the crystallizing-point. Citric acid forms colorless, prismatic crystals, which have a pure, and agreeable acid taste; they dissolve, with great ease, in both hot and cold water; the solution strongly reddens litmus, and, when long kept, is subject to spontaneous change.

Citric acid is tribasic; its formula in the gently dried and anhydrous silver-salt is, $C_{12}H_5O_{11}$. The hydrated acid crystallizes with two different quantities of water, assuming two different forms. The crystals, which separate by spontaneous evaporation, from a cold saturated solution, contain $C_{12}H_5O_{11}$, $3HO+2HO$, the last being water of crystallization; while, on the other hand, those which are deposited from a hot solution contain but 4 equivalents of water altogether, three of which are basic. Citric acid is entirely decomposed when heated with sulphuric and nitric acids; the latter converts it into oxalic acid. Caustic potash, at a high temperature, resolves it into acetic and oxalic acids.

The citrates are very numerous, the acid forming like ordinary phosphoric acid, three classes of salts, which contain respectively 3 eq. of a metallic oxide, 2 eq. of oxide and 1 eq. of basic water, and 1 eq. oxide and 2 eq. basic water, besides true sub-salts, in which the water of crystallization is, perhaps, replaced by a metallic oxide.

The citrates of the *alkalis* are soluble and crystallizable with greater or less facility; those of *baryta*, *strontia*, *lime*, *lead*, and *silver*, are insoluble.

Citric acid resembles tartaric acid in its relations to peroxide of iron; it prevents the precipitation of that substance by excess of ammonia. The citrate, obtained by dissolving the hydrated oxide in solution of citric acid, dries up to a pale brown, transparent, amorphous mass, which is not very soluble in water; an addition of ammonia increases the solubility. Citrate and ammonio-citrate of iron are elegant medicinal preparations. Very little is known respecting the composition of these curious compounds; the absence of crystallization is a great bar to inquiry.

Citric acid is sometimes adulterated with tartaric; the fraud is easily detected by dissolving the acid in a little cold water, and adding to the solution a small quantity of acetate of potash. If tartaric acid be present, a white, crystalline precipitate of cream of tartar will be produced on agitation.

ACONITIC OR EQUISETIC ACID.—When crystallized citric acid is heated in a retort until it begins to become colored, and to undergo decomposition, and the fused, glassy product, after cooling, dissolved in water, an acid is obtained, differing completely in properties from citric acid, but identical with an acid extracted from the *aconitum napellus*, and the *equisetum fluviatile*. Aconitic acid

forms a white, confusedly-crystalline mass, permanent in the air, and very soluble in water, alcohol, and ether; the solution has an acid and astringent taste. The salts of aconitic acid possesses but little interest; that of *baryta* forms an insoluble gelatinous mass; *aconitate of lime*, which has a certain degree of solubility, is found abundantly in the expressed juice of the *monkshood*, and *aconitate of magnesia* in that of the equisetum.

Hydrated aconitic acid contains C_4HO_3+HO; it is formed in the artificial process above described, by the breaking up of 1 eq. of hydrated citric acid, $C_{12}H_8O_{14}$, into 5 eq. of water, and 3 eq. of aconitic acid.

MALIC ACID.—This is the acid of apples, pears, and various other fruits; it is often associated, as already observed, with citric acid. The best process for preparing the acid in question is that of Mr. Everitt, who has demonstrated its existence, in great quantity, in the juice of the common garden rhubarb; it is accompanied by acid oxalate of potash. The rhubarb stalks are peeled, and ground or grated to pulp, which is subjected to pressure. The juice is heated to the boiling-point, neutralized with carbonate of potash, and mixed with acetate of lime; insoluble oxalate of lime falls, which is removed by filtration. To the clear and nearly colorless liquid, solution of acetate of lead is added as long as a precipitate continues to be produced. The malate of lead is collected on a filter, washed, diffused through water, and decomposed by sulphuretted hydrogen.* The filtered liquid is carefully evaporated to the consistence of sirup, and left in a dry atmosphere until it becomes converted into a solid and somewhat crystalline mass of malic acid; regular crystals have not been obtained.

Malic acid is colorless, slightly deliquescent, and very soluble in water; alcohol also dissolves it. The aqueous solution has an agreeable acid taste; it becomes mouldy, and spoils by keeping. The acid is bibasic, its formula being $C_8H_4O_8+2HO$; it forms a variety of salts, some of which are neutral, others acid. The most characteristic of these are the *acid malate of ammonia*, $NH_4O, HO, C_8H_4O_8$, which crystallizes remarkably well, and the *malate of lead*, which is insoluble in pure water, but dissolves, to a considerable extent, in warm dilute acid of any kind, and separates, on cooling, in brilliant silvery crystals, which contain water. The acid may, by this feature, be distinguished. The *acid malate of lime*, $CaO, HO, C_8H_4O_8+6HO$, is also a very beautiful salt, of free solubility in warm water. It is prepared by dissolving the sparingly-soluble *neutral* malate of lime in hot dilute nitric acid, and leaving the solution to cool.

FUMARIC AND MALEIC ACID.—If malic acid be heated in a small retort, nearly filled, it melts, emits water, and enters into ebullition; a volatile acid passes over, which dissolves in the water of the recipient. After a time, small, solid, crystalline scales make their appearance in the boiling liquid, and increase in quantity, until the whole becomes solid. The process may now be interrupted, and the contents of the retort, after cooling, treated with cold water; unaltered malic acid is dissolved out, and the new substance, having a smaller degree of solubility, is left behind; it is called *fumaric* acid from its identity with an acid extracted from the common fumitory.

Fumaric acid forms small, white, crystalline laminæ, which dissolve freely in hot water and alcohol, but require for that purpose about 200 parts of cold water; it is unchanged by hot nitric acid. When heated in a current of air, it sublimes, but in a retort, undergoes decomposition. This is a phenomenon often observed in organic bodies of small volatility. Fumaric acid forms salts,

* If the acid be required pure, crystallized malate of lead, prepared as below, must be used, the freshly-precipitated salt invariably carrying down a quantity of lime, which cannot be removed by simple washing.

which have been recently examined by M. Rieckher, and an ether, which, by the action of ammonia, yields a white amorphous, insoluble powder, called *fumaride*, which corresponds in properties and constitution with oxamide. Hydrated fumaric acid contains C_4HO_3+HO; hence it is isomeric with aconitic acid.

The volatile acid produced simultaneously with the fumaric acid is called *maleic* acid; it may be obtained in crystals by evaporation in a warm place. It is very soluble in water, alcohol, and ether; it has a strong acid taste and reaction, and is convertible by heat into fumaric acid. Hydrated maleic acid contains $C_8H_2O_6+2HO$. Maleic and fumaric acids are thus seen to have precisely the same composition; they are formed by the separation of two eq. of water from hydrated malic acid.

TANNIC AND GALLIC ACIDS.—These are substances in which the acid character is much less strongly marked than in the preceding bodies; they constitute the astringent principles of plants, and are widely diffused, in one form or other, through the vegetable kingdom. It is possible that there may be several distinct modifications of tannic acid which differ among themselves in some particulars. The astringent principle of oak-bark and nut-galls, for example, is found to precipitate per-salts of iron bluish-black, while that from the leaves of the sumach and tea-plant, as well as infusions of the substances known in commerce under the names of *kino* and *catechu*, are remarkable for giving, under similar circumstances, precipitates which have a tint of green. The color of a precipitate is, however, too much influenced by external causes to be relied upon as a proof of essential difference. Unfortunately, the tannic acid or acids refuse to crystallize; one most valuable test of individuality is therefore lost.

After the reaction with per-salt of iron, the most characteristic feature of tannic acid and the other astringent infusions referred to, is that of forming insoluble compounds with a great variety of organic, and especially animal, substances, as solutions of starch and gelatine, solid muscular fibre and skin, &c., which then acquire the property of resisting putrefaction; it is on this principle that leather is manufactured. Gallic acid, on the contrary, is useless in the operation of tanning.

Fig. 163.

Tannic acid of the oak.—This substance may be prepared from nut galls, which are excrescences produced on the leaves of a species of oak, the *quercus infectoria*, by the puncture of an insect, by the elegant and happy method of M. Pelouze. A glass vessel, having somewhat the figure of that represented in the margin, is loosely stopped at its lower extremity by a bit of cotton wool, and half or two-thirds filled with powdered Aleppo-galls. Ether, prepared in the usual manner by rectification, and containing, as it invariably does, a little water, is then poured upon the powder, and the vessel loosely stopped. The liquid, which after some time collects in the receiver below, consists of two distinct strata; the lowest, which is almost colorless, is a very strong solution of nearly pure tannic acid in water; the upper, consists of ether holding in solution gallic acid, coloring matter, and other impurities. The carefully-separated heavy liquid is placed to evaporate over a surface of oil of vitriol in the vacuum of the air-pump. Tannic acid, or *tannin*, thus obtained, forms a slightly yellowish, friable, porous mass, without the slightest tendency to crystallization. It is very soluble in water, less so in alcohol, and very slightly soluble in ether. It reddens litmus, and possesses a pure astringent taste without bitterness.

A strong solution of this substance mixed with mineral acids gives rise to precipitates, which consist of combinations of the tannic acid with the acids in question; these compounds are freely soluble in pure water, but scarcely so in acid solutions. Tannic acid precipitates albumen, gelatine, salts of the vegeto-alkalis, and several other substances; it forms soluble compounds with the alkalis, which, if excess of base be present, rapidly attract oxygen and become brown by destruction of the acid; the tannates of *baryta*, *strontia*, and *lime*, are sparingly soluble, and those of the oxides of *lead* and *antimony*, insoluble. Proto-salt of iron is unchanged by solution of tannic acid; per-salt, on the contrary, gives with it a deep bluish-black precipitate which is the basis of writing-ink; hence the value of an infusion of tincture of nut-galls as a test for the presence of that metal.

Tannic acid, carefully dried, contains $C_{18}H_5O_9+3HO$.

Tannic acid, closely resembling that obtained from galls, may be extracted by cold water from *catechu;* hot water dissolves out a substance having feeble acid properties, termed *catechin.* This latter compound, when pure, crystallizes in fine colorless needles, which melt when heated, and dissolve very freely in boiling water, but scarcely at all in the cold. Catechin dissolves also in hot alcohol and ether. The aqueous solution acquires a red tint by exposure to air, and precipitates acetate of lead and corrosive sublimate white, reduces nitrate of silver on the addition of ammonia, but fails to form insoluble compounds with gelatine, starch and the vegeto-alkalis. It strikes a deep green color with peroxide-salt of iron. This body is said to be convertible by heat into tannic acid.

The formula which has been assigned to catechin is $C_{15}H_6O_6$.

Japonic and *rubinic* acids are formed by the action of alkali in excess upon catechin; the first in the caustic condition, and the second when in the state of carbonate. Japonic acid is a black and nearly insoluble substance, soluble in alkalis and precipitated by acids, containing $C_{24}H_8O_8+HO$; it is, perhaps, identical with a black substance of acid properties formed by M. Péligot by heating grape-sugar with hydrate of baryta. Rubinic acid has been but little studied; it is said to form red insoluble compounds with the earths and certain oxides of the metals.

GALLIC ACID.—Gallic acid is not nearly so abundant as tannic acid; it seems to be produced by an alteration of the latter. A solution of tannic acid in water exposed to the air, gradually absorbs oxygen, and deposits crystals of gallic acid, formed by the destruction of the tannic acid. The simplest method of preparing this acid in quantity is to take powdered nut-galls, which, when fresh and of good quality, contain 30 or 40 per cent. of tannic acid, with scarcely more than a trace of gallic, to mix this powder with water to thin paste, and to expose the mixture to the air in a warm situation for the space of two or three months, adding water from time to time to replace that lost by drying up. The mouldy, dark-colored mass produced may then be strongly pressed in a cloth, and the solid portion boiled in a considerable quantity of water. The filtered solution deposits on cooling abundance of gallic acid, which may be drained and pressed, and finally purified by re-crystallization. It forms small, feathery, and nearly colorless crystals, which have a beautiful silky lustre; it requires for solution 100 parts of cold, and only 3 parts of boiling water; the solution has an acid and astringent taste, and is gradually decomposed by keeping. Gallic acid does not precipitate gelatine; with proto-salt of iron no change is produced, but with per-salt a deep bluish-black precipitate falls, which disappears when the liquid is heated from the reduction of the peroxide of iron to protoxide at the expense of the gallic acid.

The salts of gallic acid have been but little studied; those of the alkalis are

soluble, and readily destroyed by oxidation in presence of excess of base, the solution acquiring after some time a nearly black color; the gallates of most of the other metallic oxides are insoluble.

Gallic acid, dried at 212°, contains C_7HO_3+2HO; the crystals contain an additional equivalent of water.

The insoluble residue of woody fibre and other matters, from which the gallic acid has been withdrawn by boiling water, contains a small quantity of another acid substance, which may be extracted by an alkali, and afterwards precipitated by an addition of hydrochloric acid, as a grayish insoluble powder. It contains $C_7H_2O_4$, when dried at 248°, or gallic acid *minus* 1 eq. of water. The term *ellagic acid* is given to this substance. M. Pelouze once observed its conversion into ordinary gallic acid.

The conversion of tannic into gallic acid by oxidation is accompanied by a disengagement of carbonic acid, the volume of which equals that of the oxygen absorbed; the oxidizing action must therefore be confined to the carbon, and may perhaps be thus represented—

$$\left.\begin{array}{ll}\text{1 eq. tannic acid} & C_{18}H_8O_{12}\\ \text{8 eq. oxygen} \quad . & O_8\end{array}\right\} = \left\{\begin{array}{ll}\text{2 eq. gallic acid} & C_{14}H_6O_{10}\\ \text{2 eq. water} \quad . & H_2O_2\\ \text{4 eq. carbonic acid} & C_4 \quad O_8\end{array}\right.$$

$$C_{18}H_8O_{20} \qquad\qquad C_{18}H_8O_{20}$$

Much of the gallic acid is subsequently destroyed, in all probability only a part of that first produced escaping.

The changes which gallic acid suffers when exposed to heat are very interesting. Heated in a retort by means of an oil-bath, the temperature of which is steadily maintained at 420°, or thereabouts, it is resolved into carbonic acid, and a new acid which sublimes into the neck of the retort in brilliant, crystalline plates, of the most perfect whiteness; an insignificant residue of black matter remains behind. The term *pyrogallic acid* is given to the volatile product. It dissolves with facility in water, but the solution cannot be evaporated without blackening and decomposition; it communicates a blackish-blue color to salts of the protoxide of iron, and reduces those of the peroxide to the state of protoxide. The acid characters of this substance are very indistinct. Pyrogallic acid contains $C_6H_3O_3$.

When dry gallic acid is suddenly heated to 480°, or above, it is decomposed into carbonic acid, water, and a second new acid, the *metagallic*,* which remains in the retort as a black, shining mass resembling charcoal; a few crystals of pyrogallic acid are formed at the same time. Metagallic acid is insoluble in water, but dissolves in alkalis, and is again precipitated as a black powder by the addition of an acid. It combines with the oxide of lead and silver, and is composed of $C_6H_2O_2$. Pyrogallic acid, also, exposed to the requisite temperature, yields metagallic acid, with separation of water.

Tannic acid, under similar circumstances, furnishes the same products as gallic acid. Dr. Stenhouse has shown that pyrogallic acid may be procured in considerable quantity by carefully heating the dried aqueous extract of gall-nuts in Dr. Mohr's subliming apparatus already described.† All these changes admit of simple explanation.

* Pelouze, Ann. Chim. et Phys., liv. p. 337.
† Mem. Chem. Soc. of London, i. p. 127.

$$\overbrace{C_7H_3O_5}^{\text{Dry gallic acid.}} = \overbrace{C_6H_3O_3}^{\text{Pyrogallic acid.}} \text{ and } \overbrace{CO_2}^{\text{Carbonic acid.}}$$

$$\overbrace{C_6H_3O_3}^{\text{Pyrogallic acid.}} = \overbrace{C_6H_2O_2}^{\text{Metagallic acid.}} \text{ and } \overbrace{HO}^{\text{Water.}}$$

$$\overbrace{C_{54}H_{24}O_{36}}^{\text{Tannic acid, 3 eq.}} = \overbrace{C_{42}H_{18}O_{30}}^{\text{6 eq. gallic acid.}} \text{ and } \overbrace{C_{12}H_6O_6}^{\text{2 eq. pyrogallic acid.}}.$$

These phenomena present admirable illustrations of the production of pyrogen acids by the agency of heat.

SECTION IV.

AZOTIZED ORGANIC PRINCIPLES OF SIMPLE CONSTITUTION.

CYANOGEN, ITS COMPOUNDS AND DERIVATIVES.

CYANOGEN* forms the most perfect type of a quasi-simple salt-radical that chemistry presents, as kakodyle does of the basyle class; it is interesting also from being the first-discovered body of the kind.

Cyanogen may be prepared with the utmost ease by heating in a small retort of hard glass the salt called *cyanide of mercury*, previously reduced to powder, and well dried. The cyanide undergoes decomposition, like the oxide under similar circumstances, yielding metallic mercury, a small quantity of a brown substance of which mention will again be made, and cyanogen itself, a colorless, permanent gas, which must be collected over mercury. It has a pungent and very peculiar odor, remotely resembling that of peach-kernels, or hydrocyanic acid; exposed while at the temperature of 45° to a pressure of 3·6 atmospheres, it condenses to a thin, colorless, transparent liquid.† Water dissolves 4 or 5 times its volume of this gas, and alcohol a much larger quantity; the solution rapidly decomposes, yielding ammonia, brown insoluble matter, and other products. Cyanogen is inflammable; it burns with a beautiful purple, or peach-blossom colored flame, generating water and carbonic acid. The specific gravity of this gas is 1·806; it is composed of carbon and nitrogen in the proportion of 2 equivalents of the former to 1 equivalent of the latter, or C_2N; this is easily proved by mixing it with twice its measure of pure oxygen, and firing the mixture in the eudiometer; carbonic acid is formed equal in volume to the oxygen employed, and a volume of nitrogen, equal to that of the cyanogen, is set free. Cyanogen, in its capacity of quasi-element, is designated by the symbol Cy.

PARACYANOGEN.—This is the brown or blackish substance above referred to, which is always formed in small quantity when cyanogen is prepared by heating the cyanide of mercury, and probably also, by the decomposition of solutions of cyanogen, and of hydrocyanic acid. It is insoluble in water and alcohol, is dissipated by a very high temperature, and contains, according to Professor Johnston, carbon and nitrogen in the same proportions as in cyanogen.

CYANIDE OF HYDROGEN; HYDROCYANIC OR PRUSSIC ACID. HCy.—This very important compound, so remarkable for its poisonous properties, was discovered as early as 1782, by Scheele. It may be prepared in a state of purity, and anhydrous, by the following process.—A long glass tube, filled with dry cyanide of mercury, is connected by one extremity with an arrangement for furnishing dry sulphuretted-hydrogen gas, while a narrow tube attached to the other end is made to pass into a narrow-necked phial plunged into a

* So called from κυανος, blue, and γεννάω, I generate.

† By intense cold it becomes a transparent and crystalline solid, melting at 30°. Faraday.—R. B.

freezing mixture. Gentle heat is applied to the tube, the contents of which suffer decomposition in contact with the gas, sulphuret of mercury, and cyanide of hydrogen being produced; the latter is condensed in the receiver to the liquid form. A little of the cyanide of mercury should be left undecomposed to avoid contamination of the product by sulphuretted-hydrogen. The pure acid is a thin, colorless, and exceedingly volatile liquid, which has a density of ·7058 at 45°, boils at 79° F., and solidifies, when cooled to 0°; its odor is very powerful, and most characteristic, much resembling that of peach-blossoms, or bitter-almond oil; it has a very feeble acid reaction, and mixes with water and alcohol in all proportions. In the anhydrous state, this substance constitutes one of the most formidable poisons known, and even when largely diluted with water, its effects upon the animal system are exceedingly energetic; it is employed, however, in medicine in very small doses. The inhalation of the vapor should be carefully avoided in all experiments in which hydrocyanic acid is concerned, as it produced headache, giddiness, and other disagreeable symptoms; ammonia and chlorine are the best antidotes.

The acid in its pure form cannot be preserved; even when enclosed in a carefully-stopped bottle it is observed after a very short time to darken, and eventually to deposit a black substance containing carbon, nitrogen, and perhaps hydrogen; ammonia is formed at the same time, and probably other products. Light favors this decomposition. Even in a dilute condition it is apt to decompose, becoming brown and turbid, but not always with the same facility, some samples resisting change for a great length of time, and then suddenly solidifying to a brown, pasty mass in a few weeks.

When hydrocyanic acid is mixed with concentrated mineral acids, the hydrochloric for example, the whole solidifies to a crystalline paste of sal-ammoniac and hydrated formic acid; a reaction which is explained in a very simple manner, 1 eq. of hydrocyanic acid, and 3 eq. of water, yielding 1 eq. of ammonia, and 1 eq. of formic acid.

$$C_2N,H \text{ and } 3\,HO = NH_3 \text{ and } C_2HO_3.$$

On the other hand, when dry formiate of ammonia is heated to 392°, it is almost entirely converted into hydrated hydrocyanic acid.*

$$NH_4O\,,C_2HO_3 = C_2NH \text{ and } 4HO.$$

Aqueous solution of hydrocyanic acid may be had by various means. The most economical, and by far the best where considerable quantities are wanted, is to decompose at a boiling heat the yellow ferrocyanide of potassium by diluted sulphuric acid. For example, 500 grains of the powdered ferrocyanide may be dissolved in four or five ounces of warm water, and introduced into a capacious flask or globe capable of being connected by a perforated cork and wide bent tube with a Liebig's condenser well supplied with cold water; 300 grains of oil of vitriol are diluted with three or four times as much water and added to the contents of the flask; distillation is carried on until about one-half of the liquid has distilled over, after which the process may be interrupted. The theory of this process has been carefully studied by Mr. Everitt;† it is sufficiently complicated.

* Pelouze, Ann. Chim. et Phys., xlviii. p. 395.
† Phil. Magazine, Feb. 1835.

2 eq. ferro-cyanide potassium { 6 eq. carbon — Insoluble yellow salt.
6 eq. carbon
3 eq. nitrogen
3 eq. nitrogen
1 eq. potassium
3 eq. potassium
2 eq. iron

3 eq. water { 3 eq. hydrogen — 3 eq. hydrocyanic acid.
3 eq. oxygen

6 eq. sulphuric acid — 3 eq. bisulphate of potash.

The substance described in the above diagram as *insoluble yellow salt*, remains in the flask after the reaction, together with the bisulphate of potash; it contains the elements of 2 eq. cyanide of iron, and 1 eq. cyanide of potassium, but its constitution is unknown. On exposure to the air, it rapidly becomes blue.

When hydrocyanic acid is wanted for purposes of pharmacy, it is best to prepare a strong solution in the manner above described, and then, having ascertained its exact strength, to dilute it with pure water to the standard of the pharmacopœia, viz. 2 per cent. of real acid. This examination is best made by precipitating with excess of nitrate of silver, a known weight of the acid to be tried, collecting the insoluble cyanide of silver upon a small filter previously weighed, washing, drying, and lastly, re-weighing the whole. From the weight of the cyanide, that of the hydrocyanic acid can be easily calculated, an equivalent of the one corresponding to an equivalent of the other; or the weight of the cyanide of silver may be divided by 5, which will give a close approximation to the truth.

It is a common remark, that the hydrocyanic acid made from ferro-cyanide of potassium keeps better than that made by other means. The cause of this is ascribed to the presence of a trace of mineral acid. Mr. Everitt actually found that a few drops of hydrochloric acid, added to a large bulk of the pure dilute acid, preserved it from decomposition, while another portion, not so treated, became completely spoiled.

A very elegant and convenient process for the extemporaneous preparation of an acid of definite strength, is to decompose a known quantity of cyanide of potassium by solution of tartaric acid: 100 grains of crystallized tartaric acid in powder, 44 grains of cyanide of potassium, and 2 measured ounces of distilled water, shaken up in a phial for a sew seconds, and then left at rest, in order that the precipitate may subside, will yield an acid, of very nearly the required strength. A little alcohol may be added, to complete the separation of the cream of tartar; no filtration or other treatment need be employed.

The production of hydrocyanic acid from bitter-almonds has been already mentioned in connection with the history of the volatile oil. Bitter-almonds, the kernels of plums, and peaches, the seeds of the apple, the leaves of the cherry-laurel, and various other parts of plants belonging to the great natural order *rosaceæ*, yield, on distillation with water, a sweet-smelling liquid, containing hydrocyanic acid. This is probably due, in all cases, to the decomposition of the *amygdaline*, pre-existent in the organic structure. The change in question is brought about, in a very singuler manner, by the presence of a soluble azotized substance, called *emulsine* or *synaptase*, which forms a large proportion of the white pulp of both bitter and sweet almonds. This substance bears a somewhat similar relation to amygdaline that diastase, which it closely resembles in many particulars, does to starch.

Amygdaline is prepared with facility by the following process:—The paste of bitter-almonds, from which the fixed oil has been expressed, is exhausted with boiling alcohol; this coagulates and renders inactive the synaptase, while

at the same time it dissolves out the amygdaline. The alcoholic liquid is distilled in a water-bath, by which much of the spirit is recovered, and the sirupy residue diluted with water, mixed with a little yeast, and set in a warm place to ferment; a portion of sugar, present in the almonds, is thus destroyed. The filtered liquid is then evaporated to a sirupy state in a water-bath, and mixed with a quantity of alcohol, which throws down the amygdaline as a white crystalline powder; the latter is collected on a cloth filter, pressed, re-dissolved in boiling alcohol, aad left to cool. It separates in small crystalline plates, of pearly whiteness, which are inodorous, and nearly tasteless; it is decomposed by heat, leaving a bulky coal, and diffusing the odor of the hawthorn. In water, both hot and cold, amygdaline is very soluble; a hot saturated solution deposits, on cooling, brilliant prismatic crystals, which contain water.* In cold alcohol, it dissolves with great difficulty. Heated with dilute nitric acid, or a mixture of dilute sulphuric acid and peroxide of manganese, it is resolved into ammonia, bitter-almond oil, benzoic acid, formic acid, and carbonic acid; with hypermanganate of potash, it yields a mixture of cyanate and benzoate of that base.

Amygdaline is composed of $C_{40}H_{27}NO_{22}$.

Synaptase itself has never been obtained in a state of purity, or fit for analysis; it is described as a yellowish-white opaque, brittle mass, very soluble in water, and coagulable, like albumen, by heat, in which case it loses its specific property. In solution, it very soon becomes turbid and putrefies. The decomposition of amygdaline under the influence of this body may be elegantly studied by dissolving a portion in a large quantity of water, and adding a little emulsion of sweet almond; the odor of the volatile oil immediately becomes apparent, and the liquid yields, on distillation, hydrocyanic acid. The nature of the decomposition may be thus *approximatively* represented:—

$$\begin{array}{c} \text{1 eq. amygdaline,} \\ C_{40}H_{27}NO_{22} \end{array} \left\{ \begin{array}{lllll} \text{1 eq. hydrocyanic acid} & C_2 & H & N & \\ \text{2 eq. bitter-almond oil} & C_{28} & H_{12} & & O_4 \\ \quad\text{sugar} \quad . \quad . & C_6 & H_5 & & O_5 \\ \text{2 eq. formic acid} \quad . & C_4 & H_2 & & O_6 \\ \text{7 eq. water} \quad . \quad . & & H_7 & & O_7 \\ \hline & C_{40} & H_{27} & N & O_{22} \end{array} \right.$$

It may be observed, that in preparing bitter-almond oil, the paste should be well mixed with about 20 parts of warm water, and the whole left to stand some hours before distillation; the heat must be gently raised, to avoid coagulating the synaptase before it has had time to act upon the amygdaline. Almond paste thrown into boiling water, yields little or no bitter-almond oil.

Amygdalinic acid.—When amygdaline is boiled with an alkali or an alkaline earth, it is decomposed into ammonia, and a new acid called the *amygdalinic*, which remains in union with the base. This is best prepared by means of baryta-water, the ebullition being continued as long as ammonia continues to be evolved. From the solution thus obtained, the baryta may be precipitated by dilute sulphuric acid; the filtered liquid is evaporated in a water-bath. Amygdalinic acid forms a colorless, transparent, amorphous mass, very soluble in water, and deliquescent in moist air; the solution has an acid taste and reaction. It is converted by oxidizing agents into bitter almond oil, formic, and benzoic acids. The amygdalates are mostly soluble, but have been but little studied; the acid contains $C_{40}H_{26}O_{24}+HO$.

The presence of hydrocyanic acid is detected with the utmost ease; its remarkable odor, and high degree of volatility almost sufficiently characterize it.

* Liebig, in Geiger's Pharmacie, vii. p. 631.

With solution of nitrate of silver it gives a dense curdy white precipitate, much resembling the chloride, but differing from that substance in not blackening so readily by light, in being soluble in boiling nitric acid, and in suffering complete decomposition when heated in a dry state, metallic silver being left; the chloride, under the same circumstances, merely fuses, but undergoes no chemical change. The production of Prussian blue by "Scheele's test" is an excellent and most decisive experiment, which may be made with a very small quantity of the acid. The liquid to be examined is mixed with a few drops of solution of protosulphate of iron and an excess of caustic potash, and the whole exposed to the air for 10 or 15 minutes, with agitation; hydrochloric acid is then added in excess, which dissolves the oxide of iron, and, had hydrocyanic acid been present, leaves Prussian blue as an insoluble powder. This reaction becomes quite intelligible when the production of a ferrocyanide, described a few pages hence, is understood.

The most important of the metallic cyanides are the following; they bear the most perfect analogy to the haloid salts.

Cyanide of potassium. KCy.—When potassium is heated in cyanogen gas, it takes fire and burns in a very beautiful manner, yielding cyanide of the metal; the same substance is produced when potassium is heated in the vapor of hydrocyanic acid, hydrogen being liberated. If pure nitrogen gas be transmitted through a white-hot tube, containing a mixture of carbonate of potash and charcoal, a considerable quantity of cyanide of potassium is formed, which settles in the cooler portions of the tube as a white amorphous powder; carbonic oxide is at the same time extricated. If azotized organic matter of any kind, capable of furnishing ammonia by destructive distillation, as horn-shavings, parings of hides, &c., be heated to redness with carbonate of potash in a close vessel, a very abundant production of cyanide of potassium results, which cannot, however, be advantageously extracted by direct means, but in practice is always converted into ferrocyanide, which is a much more stable substance, and crystallizes better.

There are several methods by which cyanide of potassium may be prepared for use. It may be made by passing the vapor of hydrocyanic acid into a cold alcoholic solution of potash; the salt is deposited in a crystalline form, and may be separated from the liquid, pressed and dried. Ferrocyanide of potassium, heated to whiteness in a nearly close vessel, evolves nitrogen and other gases, and leaves a mixture of charcoal, carburet of iron, and cyanide of potassium, which latter salt is not decomposed unless the temperature be excessively high. Mr. Donovan recommends the use in this process of a wrought-iron mercury bottle, which is to be half filled with the ferrocyanide, and arranged in a good air-furnace, capable of giving the requisite degree of heat; a bent iron tube is fitted to the mouth of the bottle and made to dip half an inch into a vessel of water; this serves to give exit to the gas. The bottle is gently heated at first, but the temperature ultimately raised to whiteness; when no more gas issues, the tube is stopped with a cork, and, when the whole is completely cold, the bottle is cut asunder in the middle by means of a chisel and sledge-hammer, and the pure white fused salt carefully separated from the black spongy mass below, and preserved in a well-stopped bottle; the black substance contains much cyanide, which may be extracted by a little cold water.* It would be better, perhaps, in the foregoing process, to deprive the ferrocyanide of potassium of its water of crystallization before introducing it into the iron vessel.

Professor Liebig has lately published† a very easy and excellent process

* Pharmaceutical Journal, ii. p. 573.
† Mem. Chem. Soc. of London, i. p. 94.

for making cyanide of potassium, which does not, however, yield it pure, but mixed with cyanate of potash. For many of the applications of cyanide of potassium, as for example, electro-plating and gilding, for which a considerable quantity is now required, this impurity will be of no consequence. 8 parts of ferrocyanide of potassium are rendered anhydrous by gentle heat, and intimately mixed with 3 parts of dry carbonate of potash: this mixture is thrown into a red hot earthen crucible, and kept in fusion, with occasional stirring, until gas ceases to be evolved, and the fluid portion of the mass becomes colorless. The crucible is left at rest for a moment, and then the clear salt decanted from the heavy black sediment at the bottom, which is principally metallic iron in a state of minute division. In this experiment, 2 eq. of ferrocyanide of potassium and 2 eq. carbonate of potash, yield 5 eq. cyanide of potassium, 1 eq. cyanate of potash, 2 eq. iron, and 2 eq. carbonic acid. The product may be advantageously used, instead of ferrocyanide of potassium, in the preparation of hydrated hydrocyanic acid, by distillation with diluted oil of vitriol.

Cyanide of potassium forms colorless, cubic or octahedral crystals, deliquescent in the air, and exceedingly soluble in water; it dissolves in boiling alcohol, but separates in great measure on cooling. It is readily fusible, and undergoes no change at a moderate red, or even white heat, when excluded from air; otherwise, oxygen is absorbed and the cyanide of potassium becomes cyanate of potash. Its solution always presents an alkaline reaction, and exhales when exposed to the air the smell of hydrocyanic acid; it is decomposed by the feeblest acids, even the carbonic acid of the atmosphere, and when boiled in a retort, is slowly converted into formiate of potash, with separation of ammonia. This salt is anhydrous; it is said to be as poisonous as hydrocyanic acid itself.

Cyanide of potassium has been derived from a curious and unexpected source. In some of the iron-furnaces in Scotland where raw-coal is used for fuel with the hot blast, a saline-looking substance is occasionally observed to issue in a fused state, from the tuyere-holes of the furnace, and concrete on the outside. This proved, on examination by Dr. Clark, to be principally cyanide of potassium.

Cyanide of sodium, $NaCy$, is a very soluble salt, corresponding closely with the foregoing, and obtained by similar means.

Cyanide of ammonium. NH_4Cy.—This is a colorless, crystallizable, and very soluble substance, prepared by distilling a mixture of cyanide of potassium and sal-ammoniac, or by mingling the vapor of anhydrous hydrocyanic acid with ammoniacal gas, or lastly, according to the observation of M. Langlois,* by passing ammonia over red-hot charcoal. It is very soluble in water, subject to spontaneous decomposition, and is highly poisonous.

Cyanide of mercury. $HgCy$.—One of the most remarkable features in the history of cyanogen is its powerful attraction for certain of the less oxidable metals, as silver, and more particularly, mercury and palladium. Dilute hydrocyanic acid dissolves finely-powdered red oxide of mercury with the utmost ease; the liquid loses all odor, and yields on evaporation crystals of cyanide of mercury. Cyanide of potassium is in like manner decomposed by red oxide of mercury, hydrate of potash being produced. Cyanide of mercury is generally prepared from common ferrocyanide of potassium; 2 parts of the salt are dissolved in 15 parts of hot water, and 3 parts of dry sulphate of mercury added; the whole is boiled for 15 minutes, and filtered hot from the oxide of iron, which separates. The solution, on cooling, deposits the new salt in crystals. Cyanide of mercury forms white, translucent prisms, much

* Ann. Chim. et Phys., 3d series, i. p. 111.

resembling those of corrosive sublimate; it is soluble in 8 parts of cold water, and in a much smaller quantity at a high temperature, and also in alcohol. The solution has a disagreeable metallic taste, is very poisonous, and is not precipitated by alkalis. Cyanide of mercury is useful in the laboratory as a source of cyanogen.

CYANIDE OF SILVER, AgCy, has been already described; *cyanide of zinc*, ZnCy, is a white insoluble powder, prepared by mixing acetate of zinc with hydrocyanic acid. *Cyanide of cobalt*, CoCy, is obtained by similar means; it is dirty-white and insoluble. *Cyanide of palladium* forms a pale, whitish precipitate when the chloride of that metal is mixed with a soluble cyanide, including that of mercury. *Cyanide of gold*, Au_2Cy_3, is yellowish-white and insoluble, but freely dissolved by solution of cyanide of potassium. *Protocyanide of iron* has not been obtained, from the tendency of the metal to pass into the radical and generate a *ferrocyanide*. An insoluble green compound containing FeCy, Fe_2Cy_3 was formed by M. Pelouze by passing chlorine gas into a boiling solution of ferrocyanide of potassium.

CYANIC AND CYANURIC ACIDS.—These are two remarkable isomeric bodies, related in a very close and intimate manner, and presenting phenomena of great interest. Cyanic acid is the true oxide of cyanogen; it is formed in conjunction with cyanide of potassium, when cyanogen gas is transmitted over heated hydrate or carbonate of potash, or passed into a solution of the alkaline base, the reaction resembling that by which chlorate of potash and chloride of potassium are generated when the oxide and the salt-radical are presented to each other. Cyanate of potash is, moreover, formed when the cyanide is exposed to a high temperature with access of air; unlike the chlorate, it bears a full red heat without decomposition.

Hydrated cyanic acid, CyO, HO, is procured by heating to dull redness in a hard glass retort connected with a receiver cooled by ice, cyanuric acid, deprived of its water of crystallization. The cyanuric acid is resolved, without any other product, into hydrated cyanic acid, which condenses in the receiver to a limpid, colorless liquid, of exceedingly pungent and penetrating odor, like that of the strongest acetic acid; it even blisters the skin. When mixed with water, it decomposes almost immediately, giving rise to bicarbonate of ammonia.

$$C_2N\ O,\ HO,\ \text{and}\ 2HO = C_2O_4\ \text{and}\ NH_3.$$

This is the reason why the hydrated acid cannot be separated from a cyanate by a stronger acid. A trace of cyanic acid, however, always escapes decomposition, and communicates a pungent smell to the carbonic acid evolved. The cyanates may thus be easily distinguished.

The pure hydrated cyanic acid cannot be preserved; shortly after its preparation, it changes spontaneously, with sudden elevation of temperature into a solid, white, opaque, amorphous substance, called *cyamelide*. This curious body has the same composition as hydrated cyanic acid; it is insoluble in water, alcohol, ether, and dilute acids; it dissolves in strong oil of vitriol by the aid of heat, with evolution of carbonic acid and production of ammonia; boiled with solution of caustic alkali, it dissolves, ammonia is disengaged, and a mixture of cyanate and cyanurate of the base generated. By dry distillation, it is again converted into the hydrate of cyanic acid.

CYANATE OF POTASH. KO, CyO.—The best method of preparing this salt is, according to Liebig, to oxidize cyanide of potassium by means of litharge. The cyanide, already containing a portion of cyanate, described p. 369, is remelted in an earthen crucible, and finely powdered protoxide of lead added by small portions; the oxide is instantaneously reduced, and the metal, at first in a state of minute division, ultimately collects to a fused globule at the

bottom of the crucible. The salt is poured out, and when cold, powdered and boiled with alcohol; the hot filtered solution deposits crystals of cyanate of potash on cooling. The great de-oxidizing power exerted by cyanide of potassium at a high temperature promises to render it a valuable agent in many of the finer metallurgic operations.

Another method of preparing the cyanate is to mix dried and finely-powdered ferrocyanide of potassium with half its weight of equally dry peroxide of manganese; to heat this mixture in a shallow iron ladle with free exposure to air and frequent stirring until the tinder-like combustion is at an end, and to boil the residue in alcohol, which extracts the cyanate of potash.

This salt crystallizes from alcohol in thin, colorless, transparent plates, which suffer no change in dry air, but on exposure to moisture become gradually converted, without much alteration of appearance, into bicarbonate of potash, ammonia being at the same time disengaged. Water dissolves the cyanate of potash in large quantity; the solution is slowly decomposed in the cold, and rapidly at a boiling heat, into bicarbonate of potash and ammonia. When a concentrated solution is mixed with a small quantity of dilute mineral acid, a precipitate falls, which consists of acid cyanurate of potash.* Cyanate of potash is reduced to cyanide of potassium by ignition with charcoal in a covered crucible.

Cyanate of potash mixed with solutions of lead and silver, gives rise to insoluble cyanates of the oxides of those metals, which are white.

Cyanate of ammonia—urea.—When the vapor of hydrated cyanic acid is mixed with excess of ammoniacal gas, a white, crystalline, solid substance is produced, which has all the characters of a true, although not neutral, cyanate of ammonia. It dissolves in water, and if mixed with an acid, evolves carbonic acid gas; with an alkali, it yields ammonia. If the solution be heated, or if the crystals be merely exposed a certain time to the air, a portion of ammonia is dissipated, and the properties of the compound completely changed. It may now be mixed with acids without the least symptom of decomposition, while cold caustic alkali, on the other hand, fails to disengage the smallest trace of ammonia. The result of this curious metamorphosis of the cyanate is a substance called *urea*, a product of the animal body, the chief and characteristic constituent of urine. This artificial formation of one of the products of organic life cannot fail to possess great interest. The properties of urea, and the most advantageous methods of preparing it will be found described a few pages hence.

Cyanuric acid.—The substance called *melam*, of which further mention will be made, is dissolved by gentle heat in concentrated sulphuric acid, the solution mixed with 20 or 30 parts of water, and the whole maintained at a temperature approaching the boiling-point, until a specimen of the liquid, on being tried by ammonia, no longer gives a white precipitate; several days are required. The liquid, concentrated by evaporation, deposits on cooling cyanuric acid, which is purified by re-crystallization. Another, and perhaps simpler method, is to heat dry and pure urea in a flask or retort; the substance melts, boils, disengages ammonia in large quantity, and at length becomes converted into a dirty-white, solid, amorphous mass, which is impure cyanuric acid. This is dissolved by the aid of heat in strong oil of vitriol, and nitric acid added by little and little until the liquid becomes nearly colorless; it is then mixed with water, and suffered to cool, whereupon the cyanuric acid separates.

Cyanuric acid in a pure state forms colorless crystals, seldom of large size, derived from an oblique rhombic prism, which effloresce in a dry atmo-

* Liebig, in Geiger's Pharmacie, i. p. 621.

sphere from loss of water. It is very little soluble in cold water, and requires 24 parts for solution at a boiling-heat; it reddens litmus freely, has no odor, and but little taste. This acid is tribasic; the crystals contain $C_6N_3O_3$, 3HO +4HO, and are easily deprived of the 4 eq. of water of crystallization. In point of stability, it offers a most remarkable contrast to its isomer, cyanic acid; it dissolves, as above indicated, in hot oil of vitriol, and even in strong nitric acid without decomposition, and in fact crystallizes from the latter in an anhydrous state, containing $C_6N_3O_3$, 3HO. Long-continued boiling with these powerful agents resolves it into ammonia and carbonic acid. The connection between cyanic acid, urea, and cyanuric acid may be thus recapitulated:

Cyanate of ammonia is converted by heat into urea.

Urea is decomposed by the same means into cyanuric acid and ammonia.

Cyanuric acid is changed by a very high temperature into hydrated cyanic acid.

In the latter reaction, 1 eq. of hydrated cyanuric acid splits into 3 eq. hydrated cyanic acid.

$$C_6N_3O_3, 3HO = 3\,(C_2NO, HO.)$$

FULMINIC ACID.—This remarkable compound has no other relation to the cyanogen group than the accidental one of identity of composition with the two preceding acids; it originates in the peculiar action exercised by hyponitrous acid upon alcohol in presence of a salt of silver or mercury. Neither absolute fulminic acid nor its hydrate have ever been obtained.

Fulminate of silver is prepared by dissolving 40 or 50 grains of silver, which need not be pure, in ¾ oz. by measure of nitric acid of sp. gr. 1·37, or thereabouts, by the aid of a little heat; a sixpence answers the purpose very well. To the highly acid solution, while still hot, 2 measured ounces of alcohol are added, and heat applied until reaction commences. The nitric acid oxidizes part of the alcohol to aldehyde and oxalic acid, becoming itself reduced to hyponitrous acid, which in turn acts upon the alcohol in such a manner as to form hyponitrous ether, fulminic acid, and water. 1 eq. of hyponitrous ether and 1 eq. of hyponitrous acid containing the elements of 1 eq. fulminic acid and 5 eq. water.

$$C_4H_5O, NO_3 \text{ and } NO_3 = C_4N_2O_2 \text{ and } 5HO.$$

The fulminate of silver slowly separates from the hot liquid in the form of small, brilliant, white, crystalline plates, which may be washed with a little cold water, distributed upon separate pieces of filter-paper in portions not exceeding a grain or two each, and left to dry in a warm place. When dry, the papers are folded up and preserved in a box or bottle. This is the only safe method of keeping the salt. Fulminate of silver is soluble in 36 parts of boiling water, but the greater part crystallizes out on cooling; it is one of the most dangerous substances to handle that chemistry presents; it explodes when strongly heated, or when rubbed or struck with a hard body, or when touched with concentrated sulphuric acid, with a degree of violence almost indescribable; the metal is reduced, and a large volume of gaseous matter suddenly liberated. Strange to say, it may when very cautiously mixed with oxide of copper, be burned in a tube with as much facility as any other organic substance. Its composition thus determined is expressed by the formula 2AgO, $C_4N_2O_2$.

The acid is evidently bibasic; when fulminate of silver is digested with caustic potash, one half of the oxide is precipitated, and a compound produced

containing $AgO, KO, C_4N_2O_2$, which resembles the neutral silver-salt, and detonates by a blow. Corresponding compounds containing soda and oxide of ammonium exist; but a pure fulminate of an alkaline metal has never been formed. If fulminate of silver be digested with water and copper, or zinc, the silver is entirely displaced, and a fulminate of the new metal produced. The zinc-salt mixed with baryta-water gives rise to a precipitate of oxide of zinc, while *fulminate of zinc and baryta*, $ZnO, BaO, C_4N_2O_2$, remains in solution. *Fulminate of mercury* is prepared by a process very similar to that by which the silver-salt is obtained; one part of mercury is dissolved in 12 parts of nitric acid and the solution mixed with an equal quantity of alcohol; gentle heat is applied and if the reaction becomes too violent, it may be moderated by the addition from time to time of more spirit; much carbonic acid, nitrogen and red vapor are disengaged, together with a large quantity of nitrous ether and aldehyde; these are sometimes condensed and collected for sale, but are said to contain hydrocyanic acid. The fulminate of mercury separates from the hot liquid, and after cooling may be purified from an admixture of reduced metal by solution in boiling water and recrystallization. It much resembles the silver-salt in appearance, properties, and degree of solubility, and contains $2Hg_2O, C_4N_2O_2$. It explodes violently by friction or percussion, but, unlike the silver-compound, merely burns with a sudden and almost noiseless flash when kindled in the open air. It is manufactured on a large scale for the purpose of charging *percussion caps*; sulphur and chlorate of potash are added, and the powder, pressed into the cap, is secured by a drop of varnish.

The relations of composition between the three isomeric acids are beautifully seen by comparing their silver salts; the first acid is mono-basic, the second bi-basic, and the third tri-basic.

Cyanate of silver	AgO, C_2NO.
Fulminate of silver	$2AgO, C_4N_2O_2$.
Cyanurate of silver	$3AgO, C_6N_3O_3$.

Chlorides of cyanogen.—Chlorine forms two compounds with cyanogen, or its elements, which are isomeric, and correspond to cyanic and cyanuric acids. *Gaseous chloride of cyanogen*, CyCl, is formed by conducting chlorine gas into strong hydrocyanic acid, or by passing chlorine over moist cyanide of mercury contained in a tube sheltered from the light. It is a permanent and colorless gas at the temperature of the air, of insupportable pungency, and soluble to a very considerable extent in water, alcohol and ether. At 0° F. it congeals to a mass of colorless crystals, which at 5° melt to a liquid whose boiling-point is 11° F. At the temperature of the air it is condensed to the liquid form under a pressure of 4 atmospheres, and when long preserved in this condition in hermetically-sealed tubes it gradually passes into the solid modification. Solid chloride of cyanogen is generated when anhydrous hydrocyanic acid is put into a vessel of chlorine gas, and the whole exposed to the sun; hydrochloric acid is formed at the same time. It forms long colorless needles, which exhale a powerful and offensive odor, compared by some to that of the excrements of mice; it melts at 284° and sublimes unchanged at a higher temperature. When heated in contact with water, it is decomposed into cyanuric and hydrochloric acids. This compound may be represented by the formula Cy_3Cl_3, or C_6N_3, Cl_3. It dissolves in alcohol and ether without decomposition.

Bromide and iodide of cyanogen correspond to the first of the preceding compounds, and are prepared by distilling bromine or iodine with cyanide of mercury. They are colorless, volatile, solid substances, of powerful odor.

FERROCYANOGEN, AND ITS COMPOUNDS.

When a solution of cyanide of potassium is digested with iron-filings at a gentle heat in an open vessel, oxygen is absorbed from the air, the iron dissolves quietly and disappears, and a highly alkaline, yellow liquid is obtained, which on evaporation deposits lemon-yellow crystals containing potassium in combination with a new salt-radical, composed of the metal iron and the elements of cyanogen; in the mother-liquor hydrate of potash is found. 3 eq. cyanide of potassium, 1 eq. iron, and 1 eq. oxygen, yield 1 eq. of the new salt, and 1 eq. of potash.

$$3KCy; Fe, \text{and } O = KO \text{ and } 2K, C_6N_3Fe.$$

The new substance is called *ferrocyanogen*, and is designated by the symbol Cfy; it is bi-basic, neutralizing 2 equivalents of metal or hydrogen, and contains *the elements of* 3 equivalents of cyanogen combined with 1 eq. of iron. It has never been isolated.

When iron in filings is heated in a small retort with solution of cyanide of potassium, it is dissolved with evolution of hydrogen, caustic potash and the new substance being generated; the oxygen in this case is derived from the decomposition of water. Sulphuret of iron and cyanide of potassium give rise, under similar circumstances, to sulphuret of potassium and ferrocyanide of potassium.

HYDROFERROCYANIC ACID. Cfy2H.—Ferrocyanide of lead or copper, both of which are insoluble, may be suspended in water, and decomposed by a stream of sulphuretted-hydrogen gas. The filtered solution evaporated in the vacuum of the air-pump over a surface of oil of vitriol, furnishes the acid in a solid form. If the aqueous solution be agitated with ether, nearly the whole of the acid separates in colorless, crystalline laminæ; it may even be made in large quantity by adding hydrochloric acid to a strong solution of ferrocyanide of potassium in water free from air, and shaking the whole with ether. The crystals may be dissolved in alcohol, and the acid again thrown down by ether, which possesses the remarkable property of precipitating this substance from solution.* Hydroferrocyanic acid differs completely from hydrocyanic acid; its solution in water has a powerfully acid taste and reaction, and decomposes alkaline carbonates with effervescence; it refuses to dissolve oxide of mercury in the cold, but when heat is applied, undergoes decomposition, forming cyanide of mercury and a peculiar compound of iron, cyanogen and oxygen, with reduction of some of the oxide. In a dry state, the acid is very permanent, but when long exposed to the air in contact with water, it becomes entirely converted into Prussian blue. This interesting substance was discovered by Mr. Porrett.

FERROCYANIDE OF POTASSIUM. $2K, Cfy+3HO$, or $2K, C_6N_3Fe+3HO$.—This most beautiful salt is manufactured on a large scale by the following process, which will be now easily intelligible:—Dry refuse animal matter of any kind is fused at a red heat with impure carbonate of potash and some iron-filings in a large iron vessel, from which the air should be excluded as much as possible; cyanide of potassium is generated in large quantity. The melted mass is afterwards treated with hot water, which dissolves out the cyanide and other salts; the cyanide being quickly converted by the oxide or sulphuret† of iron into ferrocyanide. The filtered solution is evaporated, and

* Posselt, Ann. der Chimie und Pharmacie, xlii. p. 163.

† The sulphur is derived from the reduced sulphate of the crude pearlashes used in this manufacture.

the first-formed crystals purified by re-solution. If a sufficient quantity of iron be not present, great loss is incured by the decomposition of the cyanide into formiate of potash and ammonia.

Ferrocyanide of potassium forms large, transparent, yellow crystals, derived from an octahedron with a square base; they cleave with facility in a direction parrallel to the base of the octahedron, and are tough and difficult to powder. They dissolve in 4 parts of cold, and in 2 of boiling water, and are insoluble in alcohol. They are permanent in the air, and have a mild saline taste. The salt has no poisonous properties, and in small doses, at least, is merely purgative. Exposed to a gentle heat, it loses 3 eq. of water, and becomes anhydrous; at a high temperature it yields cyanide of potassium, carburet of iron, and various gaseous products; if air be admitted, the cyanide becomes cyanate.

The ferrocyanides are often described as double salts in which protocyanide of iron is combined with other metallic cyanides, or with hydrogen. Thus hydroferrocyanic acid is written $FeCy+2HCy$, and ferrocyanide of potassium, $FeCy+2KCy+3HO$; the oxygen and hydrogen of the water of crystallization being respectively adequate to convert the metals into protoxides and the cyanogen into hydrocyanic acid. This view has the merit of simplicity, and will often prove a useful aid to the memory, but there are insuperable objections to its adoption as a sound and satisfactory theory.

Ferrocyanide of potassium is a chemical re-agent of great value; when mixed in solution with neutral or slightly acid salts of the metals proper, it gives rise to precipitates which very frequently present higher characteristic colors. In most of these compounds the potassium of the base is simply displaced by the new metal; the beautiful brown ferrocyanide of copper contains, for example, $2Cu+Cfy$ or $2Cu+C_6N_3Fe$, and that of lead, $2Pb+Cfy$. With salt of protoxide of iron, it gives a nearly white precipitate, which becomes rapidly blue by exposure to air; this may very possibly be neutral ferrocyanide of iron, $2Fe+Cfy$.

When a ferrocyanide is added to a solution of peroxide salt of iron, *Prussian blue* is produced. Although this remarkable substance has now been long known, and many elaborate researches have been made with a view of determining its exact composition, the problem cannot yet be said to be completely solved. This difficulty arises in great measure from the existence of several distinct deep blue compounds formed under different circumstances, and having many properties in common, which have been almost unavoidably confounded. The following is a summary of the account given by Berzelius, who has paid much attention to this subject.

Ordinary Prussian blue.—$C_{18}N_9Fe_7$, or $3Cfy+4Fe$.—This is best pepared by adding pernitrate of iron to solution of ferrocyanide of potassium, keeping the latter in slight excess. It forms a bulky precipitate of the most intense blue, which shrinks to a comparatively small compass when well washed and dried by gentle heat. In a dry state it is hard and brittle, much resembling in appearance the best indigo; the fresh-fractured surfaces have a beautiful copper-red lustre, similar to that produced by rubbing indigo with a hard body. Prussian blue is quite insoluble in water and dilute acids; concentrated oil of vitriol converts it into a white, pasty mass, which again becomes blue on the addition of water. Alkalis destroy the color instantly; they dissolve out a ferrocyanide, and leave oxide of iron. Boiled with water and red oxide of mercury, it yields a cyanide of the metal, and oxide of iron. Heated in the air, Prussian blue burns like tinder, leaving a residue of peroxide of iron. Exposed to a high temperature in a close vessel, it disengages water, cyanide of ammonium and carbonate of ammonia, and leaves carburet of iron. This

substance forms a very beautiful pigment, both an oil and a water-color, but has little permanency. The Prussian blue of commerce is always exceedingly impure; it contains alumina and other matters, which greatly diminish the brilliancy of the color.

The production of Prussian blue by mixing peroxide-salt of iron and ferrocyanide of potassium or sodium may be thus elucidated:—

3 eq. ferrocyanide potassium	3 eq. ferrocyanogen	Prussian blue.
	6 eq. potassium	
2 eq. pernitrate of iron. . .	4 eq. iron	
	6 eq. oxygen	
	6 eq. nitric acid	6 eq. nitrate of potash.

In the above formula no account is taken of the elements of water which Prussian blue certainly contains; in fact it must be looked upon as still requiring examination.

The theory of the beautiful test of Scheele for the discovery of hydrocyanic acid, or any soluble cyanide, will be now clearly intelligible. The liquid is mixed with protosalt of iron and excess of caustic alkali; the protoxide of iron quickly converts the alkaline cyanide into ferrocyanide. By exposure for a short time to the air, another portion of the hydrated oxide becomes peroxidized; when excess of acid is added, this is dissolved, together with the unaltered protoxide, and thus presented to the ferrocyanide in a state fitted for the production of Prussian blue.

Basic Prussian blue. $3Cfy, 4Fe+Fe_2O_3$.—This is a combination of Prussian blue with peroxide of iron; it is formed by exposing to the air the white or pale blue precipitate caused by a ferrocyanide in a solution of protosalt of iron. It differs from the preceding in being soluble in pure water, although not in a saline solution.

The blue precipitate obtained by adding pernitrate of iron to a large excess of ferrocyanide of potassium, is a mixture of insoluble Prussian blue with a compound containing that substance in union with ferrocyanide of potassium, or $3Cfy, 4Fe+2K, Cfy$. This also dissolves in water as soon as the salts have been removed by washing. The other ferrocyanides may be dispatched in a few words.

The *soda-salt*, $2Na, Cfy+12HO$, crystallizes in yellow 4-sided prisms, which are efflorescent in the air and very soluble.

Ferrocyanide of ammonium, $2NH_4, Cfy+3HO$, is isomorphous with ferrocyanide of potassium; it is easily soluble, and is decomposed by ebullition. *Ferrocyanide of barium*, $2Ba, Cfy$, prepared by double decomposition, or by boiling Prussian blue in baryta-water, forms minute, yellow, anhydrous crystals, which have but a small degree of solubility even in boiling water. The corresponding compounds of *strontium*, *calcium*, and *magnesium* are more freely soluble. The ferrocyanides of *silver*, *lead*, *zinc*, *manganese*, and *bismuth*, are white and insoluble; those of *nickel* and *cobalt* are pale green, and insoluble; and lastly, that of *copper* has a beautiful reddish brown tint.

Ferrocyanides with two basic metals are occasionally met with; when, for example, concentrated solutions of chloride of calcium and ferrocyanide of potassium are mixed, a sparingly soluble crystalline precipitate falls, containing $K, Ca+Cfy$, the salt-radical being half saturated with potassium, and half with calcium; many similar compounds have been formed.

FERRI, OR FERRIDCYANOGEN. $C_{12}N_6Fe_2$; or Cfdy.—This name is given to a substance, by some thought to be a new salt-radical, isomeric with ferrocyanogen, but differing in capacity of saturation; it has never been isolated.

Ferridcyanide of potassium is thus prepared: Chlorine is slowly passed, with agitation, into a somewhat dilute and cold solution of ferrocyanide of potassium, until the liquid acquires a deep reddish-green color, and ceases to precipitate a salt of the peroxide of iron. It is then evaporated, until a skin begins to form upon the surface, filtered, and left to cool; the salt is purified by re-crystallization. It forms regular prismatic, or sometimes tabular crystals, of a beautiful ruby-red tint, permanent in the air, and soluble in 4 parts of cold water; the solution has a dark greenish color. The crystals burn when introduced into the flame of a candle, and emit sparks.

Ferridcyanide of potassium contains $3K+Cfdy$; hence the radical is tribasic; the salt is formed by the abstraction of an equivalent of potassium from 2 eq. of the yellow ferrocyanide of potassium. It is decomposed by excess of chlorine, and by de-oxidizing agents, as sulphuretted-hydrogen. The term *red ferroprussiate of potash* is often, but very improperly, given to this substance.

Ferridcyanide of hydrogen is obtained in the form of a reddish-brown acid liquid, by decomposing ferridcyanide of lead with sulphuric acid; it is very instable, and is resolved, by boiling, into a hydrated percyanide of iron, an insoluble dark green powder, containing Fe_2Cy_3+3HO, and hydrocyanic acid. The ferridcyanides of *sodium*, *ammonium*, and of the alkaline earths are soluble; those of most of the other metals are insoluble. Ferridcyanide of potassium, added to a salt of the *peroxide* of iron, occasions no precipitate, but merely a darkening of the reddish-brown color of the solution; with protoxide of iron, on the other hand, it gives a deep blue precipitate, containing $3Fe+Cfdy$, which, when dry, has a brighter tint than that of Prussian blue; it is known under the name of *Turnbull's blue*. Hence, ferrideyanide of potassium is as excellent a test for protoxide of iron, as the yellow ferrocyanide is for the peroxide.

COBALTOCYANOGEN.—A series of compounds analogous to the preceding, containing cobalt, in place of iron, have been formed, and partially studied; a hydrogen-acid has been obtained, and a number of salts, which much resemble those of ferridcyanogen. It is to be expected that other metals of the same isomorphous family may be found capable of replacing iron in these circumstances.

SULPHOCYANOGEN; ITS COMPOUDS AND DERIVATIVES.

The elements of cyanogen combine with sulphur, forming a very important and well-defined salt-radical, called *sulphocyanogen*, which contains C_2NS_2, and is monobasic; it is expressed by the symbol Csy.

SULPHOCYANIDE OF POTASSIUM. KCsy.—Yellow ferrocyanide of potassium, deprived of its water of crystallization, is intimately mixed with half its weight of sulphur, and the whole heated to tranquil fusion in an iron pot, and kept some time in that condition. When cold, the melted mass is boiled with water, which dissolves out a mixture of sulphocyanide of potassium and sulphocyanide of iron, leaving little behind but the excess of sulphur employed in the experiment. This solution, which becomes red on exposure to the air from the oxidation of the iron, is mixed with carbonate of potash, by which the oxide of iron is precipitated, and potassium substituted; an excess of the carbonate must be, as far as possible, avoided. The filtered liquid is concentrated, by evaporation over the open fire, to a small bulk, and left to cool and crystallize. The crystals are drained, purified by re-solution, if necessary, or dried by enclosing them, spread on filter-paper, over a surface of oil of vitriol, covered by a bell-jar.

The reaction between the sulphur and the elements of the yellow salt is

easily explained: 1 eq. of ferrocyanide of potassium, and 6 eq. sulphur, yield 2 eq. sulphocyanide of potassium, and 1 eq. of sulphocyanide of iron.

$$2K, Cfy = C_6N_3Fe, 2K, \text{ and } 6S = 2(K, C_2NS_2) \text{ and } Fe, C_2NS_2.$$

The new salt crystallizes in long, slender, colorless prisms, or plates, which are anhydrous; it has a bitter, saline taste, and is destitute of poisonous properties; it is very soluble in water and alcohol, and deliquesces when exposed to a moist atmosphere. When heated, it fuses to a colorless liquid, at a temperature far below that of ignition.

When chlorine is passed into a strong solution of sulphocyanide of potassium, a large quantity of a bulky, deep yellow, insoluble substance, resembling some varieties of chromate of lead, is produced, together with chloride of potassium, which tends to choke up the tube delivering the gas; the liquid sometimes assumes a deep red tint, and disengages a pungent vapor, probably chloride of cyanogen This yellow matter may be collected on a filter, well washed with boiling water, and dried; it retains its brilliancy of tint. The term *sulphocyanogen* has generally been applied to this substance, from its supposed identity with the radical of the sulphocyanides; Mr. Parnell, however, invariably found it to contain both oxygen and hydrogen, and assigned to it a formula much more complex than that belonging to the true sulphocyanogen, namely, $C_{12}H_3N_6S_{12}O$. The yellow substance is quite insoluble in water, alcohol and ether; it dissolves in concentrated sulphuric acid, from which it is precipitated by dilution. Caustic potash also dissolves it, with decomposition; acids throw down from this solution a pale, yellow, insoluble body, having acid properties. When heated in a dry state, the so-called sulphocyanogen evolves sulphur and bi-sulphuret of carbon, and leaves a curious, pale, straw-yellow substance, called *mellon*, which contains C_6N_4, and enjoys the properties of a salt-radical, combining with hydrogen and the metals. Mellon bears a dull red heat without decomposition, but is resolved by strong ignition into a mixture of cyanogen and nitrogen gases. It is quite insoluble in water, alcohol, and dilute acids.

HYDROSULPHOCYANIC ACID, CsyH, is obtained by decomposing sulphocyanide of lead, suspended in water, by sulphuretted hydrogen. The filtered solution is colorless, very acid, and not poisonous; it is easily decomposed, in a very complex manner, by ebullition, and by exposure to the air. By neutralizing the liquid with ammonia, and evaporating very gently, to dryness, *sulphocyanide of ammonium*, NH_4, Csy, is obtained as a deliquescent, saline mass. The sulphocyanides of *sodium*, *barium*, *strontium*, *calcium*, *manganese*, and *iron*, are colorless, and very soluble; those of *lead* and *silver* are white and insoluble. A soluble sulphocyanide, mixed with a salt of the peroxide of iron, gives no precipitate, but causes the liquid to assume a deep blood-red tint, exactly similar to that caused under similar circumstances by meconic acid; hence the occasional use of sulphocyanide of potassium as a test for iron in the state of peroxide.

MELAM.—Such is the name given by Liebig to a curious buff-colored, insoluble, amorphous substance, obtained by the distillation at a high temperature of sulphocyanide of ammonium. It may be prepared, in large quantity, by intimately mixing 1 part of perfectly dry sulphocyanide of potassium with 2 parts of powdered sal-ammoniac, and heating the mixture for some time in a retort or flask; bisulphuret of carbon, sulphuret of ammonium, and sulphuretted hydrogen, are disengaged and volatilized, while a mixture of melam, chloride of potassium, and some sal-ammoniac remains; the two latter substances are removed by washing with hot water. Melam contains $C_{12}H_9N_{11}$; it dissolves in concentrated sulphuric acid, and gives, by dilution with water

and long boiling, cyanuric acid. The same substance is produced with disengagement of ammonia when melam is fused with hydrate of potash. When strongly heated, melam is resolved into mellon and ammonia.

If melam be boiled for a long time in a moderately strong solution of caustic potash, until the whole has dissolved, and the liquid be then concentrated, a crystalline substance separates on cooling, which is called *melamine*. By recrystallization it is obtained in colorless crystals, having the figure of an octahedron with rhombic base; it is but slightly soluble in cold water, fusible by heat, and volatile with trifling decomposition. It contains $C_6H_6N_6$, and acts as a base, combining with acids to crystallizable compounds. A second basic substance, called *ammeline*, very similar in properties to melamine, is found in the alkaline mother-liquor from which the melamine has separated; it is thrown down on neutralizing the liquid with acetic acid. The precipitate, dissolved in dilute nitric acid, yields crystals of nitrate of ammeline, from which the pure ammeline may be separated by ammonia. It forms a brilliant white powder of minute needles, insoluble in water and alcohol, and contains $C_6H_5N_5O_2$. When ammeline is dissolved in concentrated sulphuric acid, and the solution mixed with a large quantity of water, or better, spirit of wine, a white, insoluble, powder falls, which is designated *ammeline*, and is found to contain $C_{12}H_9N_9O_6$. When long boiled with dilute sulphuric acid, ammeline is converted into cyanuric acid and ammonia.

UREA; URIC ACID, AND ITS PRODUCTS.

These bodies are closely connected with the cyanogen-compounds, and may be most conveniently discussed in the present place.

UREA.—Urea may be extracted from its natural source, the urine, or it may be prepared by artificial means. Fresh urine is concentrated in a water-bath, until reduced to an eighth or a tenth of its original volume, and filtered through cloth from the insoluble deposit of urates and phosphates. The liquid is mixed with about an equal quantity of a strong solution of oxalic acid in hot water, and the whole vigorously agitated, and left to cool. A very copious fawn-colored crystalline precipitate of *oxalate of urea* is obtained, which may be placed upon a cloth filter, slightly washed with cold water, and pressed. This is to be dissolved in boiling-hot water, and powdered chalk added until effervescence ceases, and the liquid becomes neutral. The solution of urea is filtered from the insoluble oxalate of lime, warmed with a little animal charcoal, again filtered, and concentrated by evaporation, avoiding ebullition, until crystals form on cooling: these are purified by a repetition of the last part of the process. Urea can be extracted in great abundance from the urine of horses and cattle, duly concentrated, and from which the hippuric acid has been separated by an addition of hydrochloric acid; oxalic acid throws down the oxalate in such quantity as to render the whole semi-solid.

By artificial means, urea is produced by heating solution of cyanate of ammonia. The following method of proceeding yields it in any quantity that can be desired. Cyanate of potash, prepared by Liebig's process,* is dissolved in a small quantity of water, and a quantity of dry neutral sulphate of ammonia, equal in weight to the cyanate, added. The whole is evaporated to dryness in a water-bath, and the dry residue boiled with strong alcohol, which dissolves out the urea, leaving the sulphate of potash and the excess of sulphate of ammonia untouched. The filtered solution, concentrated by distilling off a portion of the spirit, deposits the urea in beautiful crystals of considerable magnitude.

* See page 371.

Urea forms transparent, colorless, 4-sided prisms, which are soluble in an equal weight of cold water, and in a much smaller quantity at a high temperature. It is also readily dissolved by alcohol. It is inodorous, has a cooling, saline taste, and is permanent in the air, unless the latter be very damp. When heated, it melts, and, at a higher temperature, decomposes with evolution of ammonia and cyanate of ammonia; cyanuric acid remains, which bears a much greater heat without change. The solution of urea is neutral to test-paper; it is not decomposed in the cold by alkalis or by hydrate of lime, but at a boiling heat emits ammonia, and forms a carbonate of the base. The same change happens by fusion with the alkaline hydrates. Brought into contact with nitrous acid, it is decomposed instantly into a mixture of nitrogen and carbonic acid gases; with chlorine it yields hydrochloric acid, nitrogen and carbonic acid. Crystallized urea is anhydrous; it contains $C_2H_4N_2O_2$, or the *elements of cyanate of oxide of ammonium.* It differs from carbonate of ammonia by the elements of water; hence, it might with some propriety be called *carbamide.* It is easily converted into carbonate of ammonia by assimilating the oxygen and hydrogen of 2 eq. of water. A solution of pure urea shows no tendency to change by keeping, and is not decomposed by boiling; in the urine, on the other hand, where it is associated with putrifiable organic matter, as mucus, the case is different. In putrid urine no urea can be found, but enough carbonate of ammonia to cause brisk effervescence with an acid; and if urine, in a recent state, be long boiled, it gives off ammonia and carbonic acid from the same source.

Urea acts as a salt-base; with nitric acid it forms a sparingly-soluble compound, which crystallizes, when pure, in small, indistinct, colorless plates, containing single equivalents of urea, nitric acid, and water. When colorless nitric acid is added to urine, concentrated to a fourth or a sixth of its volume, and cold, the nitrate crystallizes out in large, brilliant, yellow laminæ, which are very insoluble in the acid liquid. The production of this nitrate is highly characteristic of urea. The oxalate, when pure, crystallizes in large transparent, colorless plates, which have an acid reaction, and are sparingly soluble; it contains an equivalent of water. The other compounds of urea are more soluble.

Uric, or lithic acid.—This is a product of the animal organism, and has never been produced by artificial means. It may be prepared from human urine by concentration, and addition of hydrochloric acid; it crystallizes out after some time in the form of small, reddish, translucent grains, very difficult to purify. A much preferable method is, to employ the solid white urine of serpents, which can be easily procured; this consists almost entirely of uric acid and urate of ammonia. It is reduced to powder, and boiled in dilute solution of caustic potash; the liquid, filtered from the insignificant residue of feculent matter and earthy phosphates, is mixed with excess of hydrochloric acid, boiled for a few minutes, and left to cool. The product is collected on a filter, washed until free from chloride of potassium, and dried by gentle heat.

Uric acid thus obtained, forms a glistening, snow-white powder, tasteless, inodorous, and *very* sparingly soluble. It is seen under the microscope to consist of minute, but regular crystals. It dissolves in concentrated sulphuric acid without apparent decomposition, and is precipitated by dilution with water. By destructive distillation, uric acid yields cyanic, hydrocyanic and carbonic acids, carbonate of ammonia, and a black coaly residue, rich in nitrogen. By fusion with hydrate of potash, it furnishes carbonate and cyanate of the base, and cyanide of the alkaline metal. When treated with nitric acid, and with peroxide of lead, it undergoes decomposition in a manner to be presently described.

Uric acid is found by analysis to contain $C_{10}H_4N_4O_6$.

The only salts of uric acid that have attracted any attention are those of the

alkalis. *Urate of potash* is deposited from a hot, saturated solution of uric acid in the dilute alkali as a white, sparingly soluble concretionary mass, composed of minute needles; it requires about 500 parts of cold water for solution, is rather more soluble at a high temperature, and much more soluble in excess of alkali. *Urate of soda* resembles the salt of potash; it forms the chief constituent of gouty concretions in the joints, called *chalk-stones*. *Urate of ammonia* is also a sparingly soluble compound, requiring for the purpose about 1000 parts of cold water; the solubility is very much increased by the presence of a small quantity of certain salts, as chloride of sodium. This is the most common of the urinary deposits, forming a buff-colored, or pinkish cloud or muddiness, which disappears by re-solution when the urine is warmed; the secretion from which this is deposited has usually a slightly acid reaction. It occurs also as a calculus.

The following substances result from the oxidation of uric acid by peroxide of lead and nitric acid; they are some of the most beautiful and interesting bodies known.*

Allantoin.—Allantoin occurs ready-formed in the allantoic liquid of the fœtal calf. It is produced artificially by boiling together water, uric acid, and pure, freshly-prepared peroxide of lead; the filtered liquid, duly concentrated by evaporation, deposits crystals of allantoin on cooling, which are purified by re-solution and the use of animal charcoal. It forms small but most brilliant prismatic crystals, which are transparent and colorless, destitute of taste, and without action on vegetable colors. Allantoin dissolves in 160 parts of cold water, and in a smaller quantity at the boiling temperature. It is decomposed by boiling with nitric acid, and by oil of vitriol when concentrated and hot, being in this case resolved into ammonia, carbonic acid and carbonic oxide. Heated with concentrated solution of caustic alkalis, it is decomposed into ammonia and oxalic acid, which latter combines with the base. These reactions are explained by the analysis of the substance, which shows it to be composed of the elements of oxalate of ammonia *minus* those of three equivalents of water, or $C_4H_3N_2O_3$.

The production of allantoin from uric acid and peroxide of lead is also perfectly intelligible; 1 eq. of uric acid, 2 eq. of oxygen from the peroxide, and 3 eq. of water, contain the elements of allantoin, 2 eq. of oxalic acid, and 1 eq. of urea.

$$C_{10}H_4N_4O_6, 2O, \text{ and } 3HO = C_4H_3N_2O_3, C_4O_6 \text{ and } C_2H_4N_2O_2.$$

The insoluble matter from which the solution of allantoin is filtered consists in great part of oxalate of lead, and the mother liquor from which the crystals of allantoin have separated yields, on further evaporation, a large quantity of pure urea.

Alloxan.—This is the characteristic product of the action of concentrated nitric acid on uric acid in the cold. An acid is prepared, of sp. gr. 1·45, or thereabouts, and placed in a shallow open basin; into this a third of its weight of dry uric acid is thrown, by small portions, with constant agitation, care being taken that the temperature never rises to any considerable extent. The uric acid at first dissolves with copious effervescence of carbonic and nitrogen gases, and eventually the whole becomes a mass of white, crystalline, pasty matter. This is left to stand some hours, drained from the acid liquid in a funnel whose neck is stopped with powder and fragments of glass, and afterwards more effectually dried upon a porous tile. This is alloxan in a crude state; it is purified by solution in a small quantity of water, and crystallization.

* Wöhler and Liebig, Untersuchungen über die Natur der Harnsäure. Annalen der Pharmacie, xxvi. p. 241; also, Ann. Chim. et Phys., lxviii. p. 225.

Alloxan crystallizes with facility from a hot and concentrated solution slowly suffered to cool, in solid, hard, anhydrous crystals of great regularity, which are transparent, nearly colorless, have a high lustre, and the figure of a modified rhombic octahedron. A cold solution, on the other hand, left to evaporate spontaneously, deposits large foliated crystals, which contain 6 eq. of water; they effloresce rapidly in the air. Alloxan is very soluble in water; the solution has an acid reaction, a disagreeable astringent taste, and stains the skin, after a time, red or purple. It is decomposed by alkalis, and both by oxidizing and de-oxidizing agents; its most characteristic property is that of forming a deep blue compound with a salt of protoxide of iron and an alkali.

Alloxan contains $C_8H_4N_2O_{10}$; its production is thus illustrated: 1 eq. of uric acid, 4 eq. of water, and 1 eq. of nitric acid, contain the elements of alloxan, 2 eq. carbonic acid, 2 eq. of free nitrogen, 1 eq. of ammonia, and 1 eq. of water:—

$$C_{10}H_4N_4O_6\text{ , }4HO\text{ and }NO_5 = C_8H_4N_2O_{10}\text{ , }2CO_2\text{ , }2N\text{ , }NH_3\text{ , and }HO.$$

When to a solution of alloxan, heated to 140° F., baryta-water is added as long as the precipitate first produced redissolves, and the filtered solution is then left to cool, a substance is deposited in small, colorless, pearly crystals, which consists of baryta in combination with a new acid, the *alloxanic*. From this salt the base may be separated by the cautious addition of dilute sulphuric acid; the filtered liquid by gentle evaporation yields alloxanic acid in small radiated needles. It has an acid taste and reaction, decomposes carbonates, and dissolves zinc with disengagement of hydrogen. It contains in the hydrated state $C_4H\ N\ O_4 + HO$, and results from the decomposition of the alloxan, under the influence of the base, into 2 eq. of alloxanic acid and 2 eq. of water. The alloxanates of the alkalis are freely soluble; those of the earths dissolve in a large quantity of tepid water, and that of silver is quite insoluble, and anhydrous.

If a warm saturated solution of alloxanate of baryta be heated to ebullition, a precipitate falls, which is a mixture of carbonate and alloxanate of baryta with an insoluble salt of a second new acid, the *mesoxalic*; the solution is found to contain unaltered alloxanate of baryta, and urea. Mesoxalic acid is best prepared by slowly adding solution of alloxan to a boiling-hot solution of acetate of lead; the heavy granular precipitate of mesoxalate of lead thus produced, is washed and decomposed by sulphuretted hydrogen; urea is also formed in this experiment. Hydrate of mesoxalic acid is crystallizable; it has a sour taste and powerfully acid reaction, and resists a boiling heat; it forms sparingly soluble salts with baryta and lime, and a yellowish insoluble compound with oxide of silver, which is reduced with effervescence when gently heated. This remarkable acid contains, as hydrate, $C_3O_4 + 2HO$, and is, consequently, bi-basic; it is formed by the resolution of alloxan into urea, and 2 eq. of mesoxalic acid:

$$C_8H_4N_2O_{10} = C_2H_4N_2O_2\text{ and }2C_3O_4.$$

When ammonia in excess is added to a solution of alloxan, the whole heated to ebullition, and afterwards supersaturated with dilute sulphuric acid, a yellow, light precipitate falls, which increases in quantity as the liquid cools. This is *mykomelinic acid*; it is but feebly soluble in water, easily dissolved by alkalis, and forms a yellow compound with oxide of silver. Mykomelinic acid contains $C_8H_5N_4O_5$; it is produced by the conversion of alloxan and 2 eq. of ammonia into 1 eq. of mykomelinic acid and 5 eq. of water.

Parabanic acid.—This is the characteristic product of the action of moderately strong nitric acid on uric acid or alloxan, *by the aid of heat;* it is conveniently prepared by heating together 1 part of uric acid and 8 parts of nitric acid until the reaction has nearly ceased; the liquid is evaporated to a sirupy state, and left to cool; the acid is drained from the mother-liquor and purified by re-crystallization. Parabanic acid forms beautiful colorless, transparent, thin prismatic crystals, which are permanent in the air; it is easily soluble in water, has a pure and powerful acid taste, and reddens litmus strongly. Neutralized with ammonia, and mixed with nitrate of silver, it gives a white precipitate. Crystallized parabanic acid contains $C_6N_2O_4+2HO$; its production is thus explained:—1 eq. of uric acid, 2 eq. of water, and 4 eq. of oxygen from the nitric acid, yield 1 eq. of parabanic acid, 4 eq. of carbonic acid, and 2 eq. of ammonia; or, alloxan and four additional equivalents of oxygen furnish 1 eq. of parabanic acid, 2 eq. of carbonic acid, and 4 eq. of water.

The alkaline parabanates undergo a singular change by exposure to heat; if a solution of the acid be saturated with ammonia, boiled for a moment, and then left to cool, a substance separates in tufts of beautiful colorless needles; this is the ammonia-salt of an acid called the *oxaluric.* The hydrated acid is procured by adding an excess of dilute sulphuric acid to a hot and strong solution of oxalurate of ammonia, and cooling the whole rapidly. It forms a white, crystalline powder, of acid taste and reaction, capable of combining with bases; the salts of *baryta* and *lime* are sparingly soluble; that of *silver* crystallizes from the mixed hot solution of nitrate of silver and oxalurate of ammonia in long, silky needles. Oxaluric acid is composed of $C_6H_3N_2O_7+HO$; or the elements of 1 eq. of parabanic acid and 3 eq. of water. A solution of oxaluric acid is resolved by ebullition into free oxalic acid and oxalate of urea.

Thionuric acid.—A cold solution of alloxan is mixed with a saturated solution of sulphurous acid in water, in such quantity that the odor of the gas remains quite distinct; an excess of carbonate of ammonia, mixed with a little caustic ammonia is then added, and the whole boiled a few minutes. On cooling, *thionurate of ammonia* is deposited in great abundance, forming beautiful colorless, crystalline plates, which by solution in water and recrystallization acquire a fine pink tint. A solution of this salt gives with acetate of lead a precipitate of insoluble thionurate of the oxide of that metal, which is at first white and gelatinous, but shortly becomes dense and crystalline; from this compound the hydrated acid may be obtained by the aid of sulphuretted hydrogen. It forms a white, crystalline mass, permanent in the air, very soluble in water, of acid taste and reaction, and capable of combining directly with bases. When its solution is heated to the boiling-point it undergoes decomposition, yielding sulphuric acid and a very peculiar and nearly insoluble substance, called *uramile.* Thionuric acid is bibasic; the hydrate contains $C_8H_5N_3S_2O_{12}+2HO$; or the elements of alloxan, an equivalent of ammonia, and 2 eq. of sulphurous acid.

Uramile.—The product of the spontaneous decomposition by heat of hydrated thionuric acid. Thionurate of ammonia is dissolved in hot water, mixed with a small excess of hydrochloric acid, and the whole boiled in a flask; a white, crystalline substance begins in a few moments to separate, which increases in quantity until the contents of the vessel often become semi-solid; this is the uramile. After cooling, it is collected on a filter, washed with cold water to remove the sulphuric acid, and dried by gentle heat, during which it frequently becomes pinkish. Examined by a lens, it is seen to consist of minute acicular crystals. It is tasteless and nearly insoluble in water, but dissolves in ammonia and the fixed alkalis. The ammoniacal solution

becomes purple in the air. It is decomposed by strong nitric acid, alloxan and nitrate of ammonia being generated. Uramile contains $C_8H_5N_3O_6$; or thionuric acid *minus* the elements of 2 eq. of sulphuric acid.

When a cold saturated solution of thionurate of ammonia is mixed with dilute sulphuric acid, and evaporated in a water-bath, instead of uramile, another substance, *uramilic acid*, is formed and deposited in slender, colorless prisms, soluble in 8 parts of cold water. Uramilic acid dissolves in concentrated sulphuric acid without apparent decomposition; it has a feeble acid taste and reaction, and combines with bases. The salts of the alkalis are easily soluble; those of the earths much less so, and that of the oxide of silver is insoluble. Uramilic acid contains $C_{16}H_{10}N_5O_{15}$; 2 eq. of uramile and 3 eq. of water contain the elements of uramilic acid and 1 eq. of ammonia. It is a substance difficult of preparation.

ALLOXANTINE.—This is the chief product of the action of hot *dilute* nitric acid upon uric acid; the surest and best method of preparing it, however, is by passing a stream of sulphuretted hydrogen gas through a moderately strong and cold solution of alloxan. The impure mother-liquor from which the crystals of alloxan have separated answers the purpose perfectly well; it is diluted with a little water, and a copious stream of the gas transmitted through it. Sulphur is deposited in large quantity, mixed with a white, crystalline substance, which is the alloxantine. The product is drained upon a filter, slightly washed, and then boiled in water; the filtered solution deposits the alloxantine on cooling. Alloxantine forms small, four sided, oblique rhombic prisms, colorless and transparent; it is soluble with difficulty in cold water, but more freely at a boiling temperature. The solution reddens litmus, gives with baryta-water, a violet-colored precipitate, which disappears on heating, and when mixed with nitrate of silver, produces a black precipitate of metallic silver. Heated with chlorine or nitric acid, it is changed by oxidation to alloxan. The crystals become red when exposed to ammoniacal vapors. Alloxantine contains $C_8H_5N_2O_{10}$; or alloxan *plus* 1 equivalent of hydrogen.

This substance is readily decomposed; when a stream of sulphuretted hydrogen is passed through a boiling solution, sulphur is deposited and an acid liquid produced, supposed to contain a new acid, to which the term *dialuric* is applied. When neutralized by ammonia it yields a salt which crystallizes in colorless, silky needles, which contain $NH_4O, C_8N_2O_4 + 3HO$.—They become deep-red when heated to 212° in the air. A hot saturated solution of alloxantine mixed with a neutral salt of ammonia instantly assumes a purple color, which, however, quickly vanishes, and the liquid becomes turbid from the formation of uramile; the liquid is then found to contain alloxan and free acid. With oxide of silver, alloxantine disengages carbonic acid, reduces a portion of the metal, and converts the remainder of the oxide into oxalurate. Boiled with water and peroxide of lead, alloxantine gives urea and carbonate of lead.

MUREXIDE; PURPURATE OF AMMONIA OF DR. PROUT.—There are several different methods of preparing this magnificent compound. It may be made directly from uric acid, by dissolving that substance in dilute nitric acid, evaporating to a certain point, and then adding to the warm, but not boiling liquid, a very slight excess of ammonia. In this experiment alloxantine is first produced, which becomes afterwards partially converted into alloxan; the presence of both is requisite to the production of murexide. This process is, however, very precarious, and often fails altogether. An excellent method is to boil for a few minutes in a flask, a mixture of 1 part of dry uramile, 1 part of red oxide of mercury, and 40 parts of water, to which two or three drops of ammonia have been added; the whole assumes in a short space of time an intensely deep purple tint, and when filtered boiling-hot, deposits, on cooling,

splendid crystals of murexide, unmixed with any impurity. A third, and perhaps even still better process, is that of Dr. Gregory; 7 parts of alloxan, and 4 parts of alloxantine are dissolved in 240 parts of boiling water, and the solution added to about 80 parts of cold, strong solution of carbonate of ammonia; the liquid instantly acquires such a depth of color as to become opaque, and gives on cooling a large quantity of murexide; the operation succeeds best on a small scale.

Murexide* crystallizes in small square prisms, which by reflected light exhibit a splendid green metallic lustre, like that of the wing-cases of the rose-beetle and other insects; by transmitted light they are deep purple red. It is soluble with difficulty in cold water, much more easily at a boiling temperature, and is insoluble in alcohol and ether. Mineral acids decompose it with separation of *murexan*, and caustic potash dissolves it, with production of a most magnificent purple color, which disappears when the solution is boiled. Murexide contains, according to Liebig and Wöhler, $C_{12}H_6N_5O_8$; its production may be thus explained:—2 eq. of uramil and 3 eq. of oxygen from the oxide of mercury, give rise to murexide, 1 eq. of alloxanic acid, and 3 eq. of water.

$$2C_8H_5N_3O_6 = C_{12}H_6N_5O_8\,,\ C_4HNO_4 \text{ and } 3HO.$$

Or, on the other hand, 1 eq. of alloxan, 2 eq. of alloxantine, and 4 eq. of ammonia, yield 2 eq. of murexide and 14 eq. of water.

$$C_8H_4N_2O_{10}\,,\ 2C_8H_5N_2O_{10}, \text{ and } 4NH_3 = 2C_{12}H_6N_5O_8 \text{ and } 14HO.$$

Murexan; purpuric acid of Dr. Prout.—Liebig directs this substance to be prepared by dissolving murexide in caustic potash, heating the liquid until the color disappears, and then adding an excess of dilute sulphuric acid. It separates in colorless or slightly yellowish scales, nearly insoluble in cold water. In ammonia, it dissolves, and the solution acquires a purple color by exposure to the air, murexide being then produced. Murexan is said to contain $C_6H_4N_4O_5$. This substance, and its relation to murexide, require re-examination.

Connected with uric acid by similarity of origin, but not otherwise, are two curious and exceedingly rare substances, called *xanthic oxide*, and *cystic oxide*.

Xanthic oxide was discovered by Dr. Marcet; it occurs as an urinary calculus, of pale brown color, foliated texture, and waxy lustre, and is extracted by boiling the pulverized stone in dilute caustic potash and precipitating by carbonic acid. The xanthic oxide falls as a white precipitate, which on drying becomes pale yellow, and resembles wax when rubbed. It is nearly insoluble in water and dilute acids. Its characteristic property is to dissolve without evolution of gas in nitric acid, and to give on evaporation a deep yellow residue, which becomes yellowish-red on the addition of ammonia or solution of potash. Xanthic oxide gives on analysis $C_5H_2N_2O_2$.

Cystic oxide.—Cystic oxide calculi, although very rare, are more frequently met with than those of the preceding substance; they have a pale color, a concentric structure, and often a waxy external crust. The powdered calculus dissolves in great part, without effervescence, in dilute acids and alkalis, including ammonia; the ammoniacal solution deposits, by spontaneous evaporation, small, but beautifully colorless crystals, which have the form of six-sided prisms and square tables. It forms a saline compound with hydrochloric acid. Caustic alkalis disengage ammonia from the substance by continued ebullition. Cystic oxide contains sulphur; it is composed of $C_6H_6NS_2O_4$.

* So called from the Tyrian dye, said to have been prepared from a species of murex, —a shell-fish.

Uric acid is perfectly well characterized, even when in very small quantity, by its behavior with nitric acid. A small portion heated with a drop or two of nitric acid in a small porcelain capsule, dissolves, with copious effervescence. When this solution is cautiously evaporated nearly to dryness, and after the addition of a little water, mixed with a slight excess of ammonia, the deep red tint of murexide is immediately produced.

Impure uric acid, in a remarkable state of decomposition, is now imported into this country in large quantities, for use as a manure, under the name of *guano* or *huano*. It comes from the barren and uninhabited islets of the western coast of South America, and is the production of the countless birds that dwell undisturbed in those regions. The people of Peru have used it for ages. Guano usually appears as a pale brown powder, sometimes with whitish specks; it has an extremely offensive odor, the strength of which, however, varies very much. It is soluble in great part in water, and the solution is found to be extremely rich in oxalate of ammonia, the acid having been generated by a process of oxidation.*

* See Trans. of Chim. Soc. of London, i. p. 36.

SECTION V.

THE VEGETO-ALKALIS.

The vegeto-alkalis, or *alkaloids*, constitute a remarkable, and at present isolated, group of bodies; they are met with in various plants, always in combination with an acid, which is in many cases of peculiar nature, not occurring elsewhere in the vegetable kingdom. They are, for the most part, sparingly soluble in water, but dissolve in hot alcohol, from which they often crystallize in a very beautiful manner on cooling. The taste of these substances, when in solution, is usually intensely bitter, and their action upon the animal economy exceedingly energetic. They all contain a considerable quantity of nitrogen, and are very complicated in constitution, having high combining numbers. It is probable that these bodies are very numerous.

Morphia, or morphine.—This is the chief active principle of opium; it is the best and most characteristic type of the group, and the earliest known, dating back to the year 1803.

Opium, the inspissated juice of the poppy-capsule, is a very complicated substance, containing, besides morphia, three or four other alkaloids in very variable quantities, combined with sulphuric acid and an organic acid called the *meconic*. In addition to these, there are gummy, resinous and coloring matter, caoutchouc, &c., besides mechanical impurities, as chopped leaves. The opium of Turkey is the most valuable, and contains the largest quantity of morphia; that of Egypt and of India are considerably inferior. It has been produced in England of the finest quality, but at great cost.

If ammonia be added to a clear, aqueous infusion of opium, a very abundant buff-colored or brownish-white precipitate falls, which consists principally of morphia and narcotine, rendered insoluble by the withdrawal of the acid. The product is too impure, however, for use. The chief difficulty in the preparation of these substances is to get rid of the coloring matter, which adheres with great obstinacy, re-dissolving with the precipitates, and being again in part thrown down when the solutions are saturated with an alkali. The following method, which succeeds well upon a small scale, will serve to give the student some idea of a process very commonly pursued when it is desired to isolate at once an insoluble organic base, and the acid with which it is in combination:—A filtered solution of opium in tepid water is mixed with acetate of lead in excess; the precipitated meconate of lead is separated by a filter, and through the solution containing acetate of morphia, now freed to a considerable extent from color, a stream of sulphuretted hydrogen is passed. The filtered and nearly colorless liquid, from which the lead has thus been removed, may be warmed to expel the excess of gas, once more filtered, and then mixed with a slight excess of caustic ammonia, which throws down the morphia and narcotine; these may be separated by boiling ether, in which the latter is soluble. The meconate of lead, well-washed, suspended in water, and decomposed by sulphuretted hydrogen, yields solution of meconic acid.

Morphia and its salts are advantageously prepared, on the large scale, by the

process of Dr. Gregory. A strong infusion of opium is mixed with a solution of chloride of calcium, free from iron; meconate of lime, which is nearly insoluble, separates, while the hydrochloric acid is transferred to the alkaloids. By duly concentrating the filtered solution, the hydrochlorate of morphia may be made to crystallize, while the narcotine, and other bodies, are left behind. Repeated recrystallization, and the use of animal charcoal, then suffice to whiten and purify the salt, from which the base may be precipitated in a pure state by ammonia. Other processes have been proposed, as that of M. Thiboumëry, which consists in adding hydrate of lime in excess to an infusion of opium, by which the meconic acid is rendered insoluble, while the morphia is taken up with ease by the alkaline earth. By *exactly* neutralizing the filtered solution with hydrochloric acid, the morphia is precipitated, but in a somewhat colored state.

Morphia, when crystallized from alcohol, forms small, but very brilliant prismatic crystals, which are transparent and colorless. It requires at least 1000 parts of water for solution, tastes slightly bitter, and has an alkaline reaction. These effects are much more evident in the alcoholic solution. It dissolves in about 30 parts of boiling alcohol, and with great facility in dilute acids; it is also dissolved by excess of caustic potash or soda, but scarcely by excess of ammonia. When heated in the air, morphia melts, inflames like a resin, and leaves a small quantity of charcoal, which easily burns away.

Morphia, in powder, strikes a deep bluish color with neutral per-salts of iron, decomposes iodic acid with liberation of iodine, and forms a deep yellow or red compound with nitric acid; these reactions are by some considered characteristic.

Crystallized morphia contains $C_{35}H_{20}NO_6+2HO$.

The most characteristic and best-defined salt of this substance is the *hydrochlorate.* It crystallizes in slender, colorless needles, arranged in tufts or stellated groups, soluble in about 20 parts of cold water, and in its own weight at a boiling temperature. The crystals contain 6 eq. of water. The *sulphate, nitrate,* and *phosphate,* are crystallizable salts; the *acetate* crystallizes with great difficulty, and is usually sold in the state of a dry powder. The artificial *meconate* is sometimes prepared for medicinal use.

Narcotine.—The *marc,* or insoluble portion of opium, contains much narcotine, which may be extracted by boiling with dilute acetic acid. From the filtered solution, the narcotine is precipitated by ammonia, and afterwards purified by solution in boiling alcohol, and filtration through animal charcoal. Narcotine crystallizes in small, colorless, brilliant prisms, which are nearly insoluble in water. The basic powers of narcotine are very feeble; it is destitute of alkaline reaction, and although freely soluble in acids, refuses to form with them crystallizable compounds.

Narcotine contains $C_{48}H_{24}NO_{15}$.

Codeine.—Hydrochlorate of morphia, prepared directly from opium, as in Gregory's process, contains codeine-salt. When dissolved in water, and mixed with a slight excess of ammonia, the morphia is precipitated, and the codeine left in solution. Pure codeine crystallizes, by spontaneous evaporation, in small, colorless, transparent octahedrons; it is soluble in 80 parts of cold, and 17 of boiling water, has a strong alkaline reaction, and forms crystallizable salts.

Codeine is composed of $C_{35}H_{20}NO_5$.

Thebaine or *paramorphine, pseudomorphine, narceine,* and *meconine,* are also, at least occasionally, contained in opium; they are of small importance, and little is known respecting them.

Meconic acid is obtained from the impure meconate of lead, as already mentioned. The solution is evaporated in the vacuum of the air-pump. A

more advantageous method is to decompose the impure meconate of lime obtained in Dr. Gregory's morphia-process, by warm, dilute hydrochloric acid; to separate the crystals of acid meconate of lime, which form on cooling, and to repeat this operation until the whole of the base has been removed, which may be known by the acid being entirely combustible, without residue, when heated in the flame of a spirit-lamp upon platinum-foil. It is with the greatest difficulty obtained free from color.

Meconic acid crystallizes in little, colorless, pearly scales, which dissolve in 4 parts of hot water. It has an acid taste and reaction, forms soluble compounds with the alkalis, and insoluble salts with lime, baryta, and the oxides of lead and silver. The most remarkable feature of this substance is its property of striking a deep blood-red color with a salt of the peroxide of iron, exactly resembling that developed, under similar circumstances, by a sulphocyanide. The meconate of iron may, however, be distinguished from the latter compound, as Mr. Everett has shown, by an addition of corrosive sublimate, which bleaches the sulphocyanide, but has little effect upon the meconate. This is a point of considerable practical importance, as in medico-legal inquiries, in which evidence of the presence of opium is sought for in complex organic mixtures, the detection of meconic acid is usually the object of the chemist; and since traces of alkaline sulphocyanide are said to be found in the saliva, it becomes very desirable to remove that source of error and ambiguity.

Crystallized meconic acid contains $C_{14}HO_{11}, 3HO+6HO$.

When a solution of meconic acid in water, or, still better, in a mineral acid, is boiled, or when the dry acid is exposed in a retort to a temperature of 400°, it is decomposed, yielding a new *bibasic* acid, the *comenic*, containing $C_{12}H_2O_8, 2HO$, which much resembles in properties meconic acid. Water and carbonic acid are at the same time extricated. At a higher temperature, comenic acid itself is resolved into a second new acid, the *pyromeconic*, which sublimes, and afterwards condenses in brilliant, colorless plates. It is monobasic, and contains $C_{10}H_3O_5, HO$.

CINCHONIA AND QUINA.—It is to these vegeto-alkalis that the valuable medicinal properties of the Peruvian barks are due. They are associated in the bark with sulphuric acid, and with a special acid, not found elsewhere, called the *kinic*. Cinchonia is contained in largest quantity in the pale bark, or *cinchona condaminea;* quina in the yellow (or calysaya) bark, or *cinchona cordifolia;* the *cinchona oblongifolia* (or red bark) contains both.

The simplest, but not the most economical method, of preparing these substances, is to add a slight excess of hydrate of lime to a strong decoction of the ground bark, in acidulated water; to wash the precipitate which ensues, and boil it in alcohol. The solution, filtered while hot, deposits the vegeto-alkali on cooling. When both bases are present, they may be separated by converting them into sulphates; the salt of quina is the least soluble of the two, and crystallizes first.

Pure cinchonia, or cinchonine, crystallizes in small, but beautifully brilliant, transparent 4-sided prisms. It is but very feebly soluble in water, dissolves readily in boiling alcohol, and has but little taste, although its salts are excessively bitter. It is a powerful base, neutralizing acids completely, and forming a series of crystallizable salts.

Quina, or quinine, much resembles cinchonia; it does not crystallize so well, however, and is much more soluble in water; its taste is intensely bitter. *Sulphate of quina* is manufactured on a very large scale for medicinal use; it crystallizes in small white needles, which give a neutral solution. The solubility of this compound is much increased by the addition of a little sulphuric acid.

Cinchonia is composed of $C_{20}H_{12}NO$, and
Quina of . . . $C_{20}H_{12}NO_2$.

A third vegeto-alkali, *chinoidine*, is by some supposed to exist in Peruvian bark.

From *cusco*, or *arica-bark*, a substance denominated *aricine*, has been extracted; it closely resembles cinchonine.

Kinic acid.—Kinate of lime is found in the solution from which the bark-alkalis have been separated by hydrate of lime, and is easily obtained by evaporation, and purified by animal charcoal. From the lime-salt the acid can be extracted by decomposing it by diluted sulphuric acid. The clear solution evaporated to a sirupy consistence deposits large, distinct crystals, which resemble those of tartaric acid. It is soluble in 2 parts of water, and contains $C_{14}H_{11}O_{11}$, HO.

Strychnia and brucia are contained in *nux vomica*, in *St. Ignatius' bean*, and in *false Angustura bark;* they are associated with a peculiar acid, called the *igasuric*. Nux vomica seeds are boiled in dilute sulphuric acid until they become soft; they are then crushed, and the expressed liquid mixed with excess of hydrate of lime, which throws down the alkalis. The precipitate is boiled in spirit of wine of sp. gr. ·850, and filtered hot. Strychnia and brucia are deposited together in a colored and impure state, and may be separated by cold alcohol, in which the latter dissolves readily.

Pure strychnia crystallizes under favorable circumstances in small, but exceedingly brilliant octahedral crystals, which are transparent and colorless. It has a very bitter taste, is slightly soluble in water, and is fearfully poisonous. It dissolves in hot, and somewhat dilute spirit, but neither in absolute alcohol, ether, nor in a solution of caustic alkali. Strychnia forms with acids a series of well-defined salts. It is composed of $C_{44}H_{23}N_2O_8$.

Brucia is easily distinguished from the preceding substance, which it much resembles in many respects, by its ready solubility in alcohol, both hydrated and absolute. It dissolves also in about 500 parts of hot water. The salts of brucia are, for the most part, crystallizable.

Brucia contains $C_{44}H_{25}N_2O_7$.

Veratria is obtained from the seeds of *veratrum sabadilla*. In its purest state it is a white, or yellowish-white powder, which has a sharp burning taste, and is very poisonous. It is remarkable for occasioning violent sneezing. It is insoluble in water, but dissolves in hot alcohol, in ether, and in acids; the solution has an alkaline reaction. Veratria contains nitrogen, but its composition is yet doubtful.*

A substance called *colchicine*, extracted from the *colchicum autumnale*, and formerly confounded with veratria, is now considered distinct; its history is yet imperfect.

Conicine, or conia, and nicotine differ from the other vegetable bases in physical characters; they are volatile oily liquids. The first is extracted from hemlock, and the second from tobacco. They agree in most of their characters, having high boiling-points, very poisonous properties, strong alkaline reaction, and the power of forming with acids crystallizable salts. The formula of nicotine is given by Ortigosa as $C_{10}H_8N$; that of conicine is uncertain.†

There are very many other bodies, more or less perfectly known, having to a certain extent the properties of a salt-base; the following statement of the names and mode of occurrence of a few of these must suffice.

* Veratria, according to M. Couerbe, is composed of $C_{34}H_{22}NO_6$.—R.B.

† For an excellent description of the whole of the vegeto-alkalis, the reader is referred to Liebig's edition of Geiger's Pharmacie, vol. i. p. 1159.

Hyoscyamine.—A white, crystallizable substance, from *hyoscyamus niger.*

Daturine.—A colorless, crystalline body, from *datura stramonium.*

Atropine.—Colorless needles, from *atropa belladonna.*

Stramonine.—Colorless acicular crystals, from *datura stramonium.*

Solanine.—A pearly, crystalline substance, from various solanaceous plants.

Aconitine.—A glassy, transparent mass, from *aconitum napellus.*

Delphinine.—A yellowish, fusible substance, from the seeds of *delphinium staphisagria.*

Emetine.—A white and nearly tasteless powder from ipecacuanha root.

Curarine.—The arrow-poison of central America.

There exists an extensive series of neutral, usually bitter, and sometimes poisonous vegetable principles, of which a full account will be found in the work already referred to. Some of these are destitute of nitrogen. Two of the number, salicine and phloridzine, have been already described; the most important of the remainder are the following:—

GENTIANINE.—The bitter principle of the gentian-root, extracted by ether. It crystallizes in golden-yellow needles, is sparingly soluble in cold water, more soluble in hot water, and freely dissolved by alcohol and ether. Its composition in unknown.

POPULINE.—This substance closely resembles salicine in appearance and solubility, but has a penetrating sweet taste; it is found accompanying salicine in the bark and leaves of the aspen.

DAPHNINE.—Extracted from the bark of the *daphne mezereum;* it forms colorless, radiated needles, freely soluble in hot water, alcohol and ether.

HESPERIDINE.—A white, silky tasteless substance, obtained from the spongy part of oranges and lemons. It dissolves in 60 parts of hot water; also in alcohol and ether.

ELATERINE.—The active principle of *momordica elaterium.* It is a white, silky, crystalline powder, insoluble in water. It has a bitter taste, and excessively violent purgative properties. Alcohol, ether, and oils dissolve it. Exposed to heat, it melts and afterwards volatilizes.

PIPERINE.—A colorless, or slightly yellow crystallizable principle, extracted from pepper by the aid of alcohol. It is insoluble in water.

ANTIARINE.—The poisonous principle of the *upas antiar.* It forms small, pearly crystals, soluble in 27 parts of boiling water, and also in alcohol, but scarcely so in ether; it cannot be sublimed without decomposition. Introduced into a wound, it rapidly brings on vomiting, convulsions, and death. Antiarine contains $C_{14}H_{10}O_5$.

PICROTOXINE.—It is to this substance that *cocculus indicus* owes its active properties. Picrotoxine forms small colorless, stellated needles, of inexpressibly bitter taste, which dissolve in 25 parts of boiling water, and in 3 parts of boiling alcohol. It contains, according to MM. Pelletier and Caventou, $C_{12}H_7O_5$.

ASPARAGINE.—This, and the two following, are azotized bodies. Asparagine is found in the root of the marsh-mallow, in asparagus sprouts, and in several other plants. The mallow-roots are chopped small, and macerated in the cold with milk of lime; the filtered liquid is precipitated by carbonate of ammonia, and the clear solution evaporated in a water-bath to a sirupy state. The impure asparagine which separates after a few days, is purified by re-crystallization. Asparagine forms brilliant, transparent, colorless crystals, which have a faint cooling taste, and are freely soluble in water, especially when hot. When dissolved in a saccharine liquid, which is afterwards made to ferment; when heated with water under pressure in a close vessel; or when

boiled with an acid or an alkali, it is converted into ammonia and a new acid, the *aspartic*. Asparagine contains $C_8H_8N_2O_6$, and aspertic acid $C_8H_5NO_6$.

CAFFEINE, OR THEINE.—This remarkable substance occurs in three articles of domestic life, infusions of which are used as a beverage over the greater part of the known world, namely tea and coffee, and the leaves of the *ilex paraguayensis*; it will probably be found in other plants. A decoction of common tea, or of raw coffee-berries, previously crushed, is mixed with excess of solution of subacetate of lead. The solution, filtered from the copious yellow or greenish precipitate, is treated with sulphuretted hydrogen to remove the lead, filtered, evaporated to a small bulk, and neutralized by ammonia. The caffeine crystallizes out on cooling, and is easily purified by animal charcoal. It forms tufts of delicate, white, silky needles, which have a bitter taste, melt when heated with loss of water, and sublime without decomposition. It is soluble in about 100 parts of cold water, and much more easily at a boiling heat, or if an acid be present. Alcohol also dissolves it, but not easily. Caffeine contains $C_8H_5N_2O_2$.

THEOBROMINE.—The seeds of the *theobroma cacao*, or cacao nuts, from which chocolate is prepared, contain a crystallizable principle to which the preceding name is given. It is extracted in the same manner as caffeine, and forms a white, crystalline powder, which is much less soluble than the last-named substance. It contains $C_9H_5N_3O_4$.

SECTION VI.

ORGANIC COLORING PRINCIPLES.

THE organic coloring principles are substances of very considerable practical importance in relation to the arts; several of them too have been made the subjects of extensive and successful chemical investigation. With the exception of one red dye, cochineal, they are all of vegetable origin.

The art of dyeing is founded upon an affinity or attraction existing between the coloring matter of the dye and the fibre of the fabric. In woolen and silk this affinity is usually very considerable, and to such tissues a permanent stain is very easily communicated, but with cotton and flax it is much weaker. Recourse is then had to a third substance, which does possess in a high degree such affinity, and with this the cloth is impregnated. Alumina, peroxide of iron, and oxide of tin, are bodies of this class.

When an infusion of some dye-wood, as log-wood for example, is mixed with alum and a little alkali, a precipitate falls, consisting of alumina in combination with coloring matter, called a *lake;* it is by the formation of this insoluble substance within the fibre, that a permanent dyeing of the cloth is effected. Such applications are termed *mordants.* Oxide of iron usually gives rise to dull, heavy colors; alumina and oxide of tin, especially the latter, to brilliant ones. It is easy to see that by applying the mordant *partially* to the cloth, by a wood-block or otherwise, a pattern may be produced, as the color will be removed by washing from the other portions.

BLUE DYES; INDIGO.—This is the most important member of the group of vegetable coloring matters; it is the product of several species of the genus *indigofera*, which grow principally in warm climates. When the leaves of these plants are placed in a vessel of water and allowed to ferment, a yellow substance is dissolved out, which by contact of air, becomes deep blue and insoluble, and finally precipitates. This, washed and carefully dried, constitutes the indigo of commerce. It is not contained ready-formed in the plant, but is produced by the oxidation of some substance there present. Neither is the fermentation essential, as a mere infusion of the plant in hot water deposits indigo by standing in the air.

Indigo comes into the market in the form of cubic cakes, which, rubbed with a hard body, exhibit a copper-red appearanee; its powder has an intensely deep blue tint. The best is so light as to swim upon water. In addition to the blue coloring matter, or true indigo, it contains at least half its weight of various impurities, among which may be noticed a red resinous matter, the *indigo-red* of Berzelius; these may be extracted by boiling the powdered indigo in dilute acid, alkali, and afterwards in alcohol.

Pure indigo is quite insoluble in water, alcohol, oils, dilute acids and alkalis; it dissolves in about 15 parts of concentrated sulphuric acid, forming a deep blue pasty mass, entirely soluble in water, and often used in dyeing; this is *sulphindigotic acid*, a compound analogous to sulphovinic acid, capable of forming with alkaline bases blue salts, which although easily soluble in pure water, are insoluble in saline solutions. If an insufficient quantity of sulphuric acid

has been employed, or digestion not long enough continued, a purple powder is left on diluting the acid mass, soluble in a large quantity of pure water. The Nordhausen acid answers better for dissolving indigo than ordinary oil of vitriol. Indigo may, by cautious management, be volatilized; it forms a fine purple vapor, which condenses in brilliant copper-colored needles. The best method of subliming this substance is, according to Mr. Taylor, to mix it with plaster of Paris, make the whole into a paste with water, and spread it upon an iron plate. 1 part indigo, and 2 parts plaster, answer very well. This, when quite dry, is heated by a spirit-lamp; the volatilization of the indigo is aided by the vapor of water disengaged from the gypsum, and the surface of the mass becomes covered with beautiful crystals of pure indigo, which may be easily removed by a thin spatula. At a higher temperature, charring and decomposition take place,

In contact with deoxidizing agents, and with an alkali, indigo suffers a very curious change; it becomes soluble and nearly colorless, perhaps returning to the same state in which it existed in the plant. It is on this principle that the dyer prepares his *indigo-vat*—5 parts of powdered indigo, 10 parts of green vitriol, 15 parts of hydrate of lime, and 60 parts of water, are agitated together in a close vessel and then left to stand. The hydrated protoxide of iron, in conjunction with an excess of lime, reduces the indigo to the soluble state; a yellowish liquid is produced from which acids precipitate the *white* or *deoxidized* indigo, which absorbs oxygen with the greatest avidity, and becomes blue and insoluble. Cloth steeped in the alkaline liquid and then exposed to the air, acquires a deep and most permanent blue tint by the deposition of solid, insoluble indigo in the substance of the fibre. Instead of the iron-salt and lime, a mixture of dilute caustic soda and grape sugar may be used; the sugar becomes oxidized to formic acid, and the indigo reduced.

The following formulæ represent the composition of the bodies described:—

Blue insoluble indigo,	.	$C_{16}H_5NO_2$
White, or reduced indigo,*	.	$C_{16}H_6NO_2$
Sulphindigotic acid .	.	$C_{16}H_4NO$, $2SO + HO$.

The products of the destructive oxidation of indigo appear to be exceedingly numerous. With nitric acid it yields *anilic* and *picric* acids. The first is prepared by the action of nitric acid diluted with 10 or 15 parts of water upon indigo. It forms colorless or slightly yellowish acicular crystals, which have a feeble acid taste, and dissolve in about 1000 parts of cold water; at a high temperature it is much more soluble. Exposed to heat, it melts and sublimes unchanged. This substance is sometimes called *indigotic* acid.

Picric, or *carbazotic acid* is procured by adding powdered indigo to 10 or 12 parts of hot nitric acid of sp. gr. 1·43, and heating the solution until the action, at first very violent, ceases; on cooling, the impure picric acid crystallizes out. When pure, it forms bright yellow crystalline scales, but slightly soluble in cold water; it has an insupportably bitter taste, stains the skin yellow, and forms with potash a salt, which has even less solubility than the free acid, crystallizes in brilliant deep-yellow needles, and explodes when heated, with extraordinary violence.

Anilic acid contains $C_{14}H_4N\,O_9$, and picric acid $C_{12}H_2N_3O_{13}$. Other substances besides indigo, as salicine, silk, wool, &c., yield picric acid by the action of nitric acid.

* Properly *hydrogenized* indigo, if the above be the correct view; white indigo may, however, be viewed as a *hydrate*, and blue indigo as an oxide, of one and the same substance.

White indigo	. . . .	$C_{16}H_5NO + HO$
Blue indigo	. . . .	$C_{16}H_5NO + O$

Chromic acid, or a mixture of sulphuric acid, water and bichromate of potash, gently heated with powdered indigo, give rise to a deep yellow-brown solution, which by due concentration and cooling deposits crystals of a substance called *isatine*. When purified, isatine forms red prismatic crystals which are but slightly soluble in cold water, and contain $C_{16}H_5NO_4$, or the elements of blue indigo, *plus* 2 eq. of oxygen. In contact with alkalis, isatine assimilates the elements of water and becomes *isatinic acid*, $C_{16}H_6NO_5$. Exposed to the action of chlorine, it yields *chlorisatine*, $C_{16}H_4NClO_4$, and *bichlorisatine*, $C_{16}H_3NCl_2O_4$; these in turn yield with caustic alkali a pair of new acids.

The destruction of the color of indigo by chlorine, in presence of water, is instantaneous, a yellow or brown matter being produced; the color cannot be again restored. Caustic alkalis, in a concentrated state, also destroy indigo; two products are formed, the *chrysanilic acid* and the *anthranilic acid*. The latter is crystallizable, has a yellow color, and contains $C_{14}H_6NO_3$. Fused hydrate of potash converts indigo into a mixture of valerianate and carbonate of potash, with evolution of ammoniacal gas and hydrogen.

Certain of the products of the action of nitric acid upon *aloes* resemble very much some of the derivatives of indigo, without, however, it seems, being identical with them. Powdered aloes, heated for a considerable time with excess of moderately strong nitric acid, yields a deep red solution, which deposits on cooling a yellow crystalline mass. This, purified by suitable means, constitutes *chrysammic acid;* it crystallizes in golden-yellow scales, which have a bitter taste, and are but sparingly soluble in water. Its potash-salt has a carmine-red tint, and exhibits a green metallic lustre, like that of murexide. The mother-liquor from which the chrysammic acid has been deposited contains a second acid, the *chrysolepic*, which also forms golden-yellow, sparingly soluble, scaly crystals. The potash-salt forms small, yellow prisms of little solubility. It explodes by heat. Chrysammic acid contains $C_{15}HN_2O_{12}$; and crysolepic acid, $C_{12}H_2N_3O_{13}$; hence it is isomeric with picric acid.

LITMUS.—Litmus is used by the dyer as a red coloring matter; the chemist employs it in the blue state as a test for the presence of acid, by which it is instantly reddened. Many lichens, when exposed in a moistened state to the action of ammonia, yield purple or blue coloring principles, which, like indigo, do not pre-exist in the plant itself. Thus, the *roccella tinctoria*, the *variolaria orcina*, the *lecanora tartarea*, &c., when ground to paste with water, mixed with putrid urine or solution of carbonate of ammonia, and left for some time freely exposed to the air, furnish the *archil*, *litmus*, and *cudbear* of commerce, very similar substances, differing chiefly in the details of the preparation. From these the coloring matter is easily extracted by water or very dilute solution of ammonia.

Fresh dye-lichens, exhausted by ether, yield a crystalline substance, which, when purified by solution in alcohol, is perfectly white; to this the name *lecanorine* has been given. It is insoluble in water, soluble with difficulty in cold alcohol, easily in hot, and also in ether, acetic acid and aqueous alkaline solutions. When dissolved in dilute caustic potash and left to stand some hours, it is resolved into carbonic acid and a new substance called *orcine;* if the solution be heated, this change occurs almost instantly; even long-continued boiling with water brings about this decomposition. By neutralizing the liquid with an acid and evaporating to a small bulk, the orcine may be obtained in large square prisms, which have a slight yellowish tint, an intensely sweet taste, and a high degree of solubility both in water and alcohol; when heated, orcine loses water, and melts to a sirupy liquid, which distils unchanged.

When ammonia is added to a solution of orcine, and the whole exposed to the air, the liquid assumes a dark-red or purple tint, by absorption of oxygen; a slight excess of acetic acid then causes the precipitation of a deep-red powder, not very soluble in water, but freely dissolving in ammonia and fixed alkalis, with a purple or violet color. This is an azotized substance, formed from the elements of the ammonia and the orcine, called *orceine;* it probably constitutes the chief ingredient of the red dye-stuff of the commercial articles before-mentioned.

Some little doubt exists respecting the exact composition of these curious bodies; the experimental results admit of more than one interpretation. The following formulæ are, perhaps, not far removed from the truth.*

Lecanorine	$C_{18}H_8O_8$
Anhydrous orcine	$C_{16}H_8O_4$
Crystallized orcine	$C_{16}H_8O_4+3HO$
Orceine	$C_{16}H_9NO_7$

Crystallized orcine, 1 eq. of ammonia, and 5 eq. of oxygen, yielding orceine, and 5 eq. of water.

In preparing test-papers for chemical use with infusion of litmus, good writing or drawing-paper, free from alum and other acid salts, should be chosen. Those sheets which after drying exhibit red spots or patches, may be reddened completely by a little dilute acetic acid, and used, with much greater advantage than turmeric-paper, to discover the presence of free alkali, which restores the blue color.

Red dyes—cochineal.—This is a little insect, the *coccus cacti*, which lives on several species of *cactus*, which are found in warm climates, and cultivated for the purpose, as in central America. The dried body of the insect yields to water and alcohol a magnificent red coloring matter, precipitable by alumina and oxide of tin; *carmine* is a preparation of this kind. The composition of cochineal-red is unknown.

Madder.—The root of the *rubia tinctorum*, cultivated in Southern France, the Levant, &c., the most permanent and valuable of the red dye-stuffs. The red coloring matter, which may be extracted by several different processes from the root, is termed *alizarine;* it forms yellowish-red acicular crystals, easily soluble in alcohol, but sparingly dissolved by boiling water. It resists the action of concentrated sulphuric acid, and may be sublimed without decomposition. Alizarine contains $C_{37}H_{12}O_{10}$.

A purple or brown, and a yellow coloring matter, also exist in madder; the latter is very soluble in water. The beautiful *Turkey-red* of cotton cloth is a madder-color; it is given by a very complicated process, of which an abstract will be found in Mr. Graham's Elements of Chemistry.

Brazil wood and *logwood* give red and purple infusions, which are largely used in dyeing; the coloring principle of logwood is termed *hematoxyline*, and has been obtained in crystals. Acids brighten these colors, and alkalis render them purple or blue.

Among yellow dyes, *quercitron bark*, *fustic wood*, and *saffron*, may be mentioned, and also *turmeric;* these all give yellow infusions to water, and furnish more or less permanent colors.

* Liebig, in Geiger's Pharmacie, i. p. 1123.

SECTION VII.

OILS AND FATS.

The oils and fats form an interesting and very natural group of substances, which have been studied with great success. The vegetable and animal fats agree so closely in every respect, that it will be convenient to discuss them under one head.

Oily bodies are divided into *volatile* and *fixed;* the former are capable of being distilled without decomposition, the latter are not. When dropped or spread upon paper, they all produce a greasy stain; in the case of a volatile oil, this stain disappears when the paper is warmed, which never happens with a fixed fatty substance. All these bodies have an attraction, more or less energetic, for oxygen; this in some cases reaches such a height as to occasion spontaneous inflammation, as in the instance of large masses of cotton or flax moistened with rape or linseed-oil. The effect of this absorption of oxygen leads to a further classification of the fixed oils into *drying* and *non-drying* oils, or those which become hard and resinous by exposure to air, and those which thicken slightly, become sour and rancid, but never solidify. To the first class belong the oils used in painting, as linseed, rape, poppy-seed, and walnut, and to the second, olive and palm oils, and all the oils and fats of animal origin. The parts of plants which contain the largest quantities of oil are, in general, the seeds. Olive-oil is, however, obtained from the fruit itself. The leaves of many plants are varnished on their upper surface with a covering of waxy fat. Among the natural orders, that of the *cruciferæ* is conspicuous for the number of oil-bearing species.

The fixed oils in general have but feeble odor, and scarcely any taste; whenever a sapid oil or fat is met with, it is invariably found to contain some volatile oily principle, as in the case of common butter. They are all insoluble in water, and but slightly soluble in alcohol, with the exception of castor oil; in ether, and in the essential oils, on the other hand, they dissolve in large quantity.

The consistence of these substances varies from that of the thinnest olive-oil to that of solid, compact suet; and this difference proceeds from the variable proportions in which the proximate solid and fluid fatty principles are associated in the natural product. All these bodies may, in fact, by mere mechanical means, or by the application of a low temperature, be separated into two, or sometimes three, different substances, which dissolve in, or mix with each other, in all proportions. Thus, olive-oil, exposed to a cold of 40° F., deposits a large quantity of crystalline solid fat, which may be separated by filtration and pressure; this is termed *margarine*, from its pearly aspect. That portion of the oil which retains its fluidity at this, or even an inferior degree of cold, has received the name of *oleine* or *elaine*. Again, a solid animal fat may, by pressure between folds of blotting-paper, be made much harder, more brittle, and more difficult of fusion. The paper becomes impregnated with a permanently-fluid oil, or oleine, while the solid part is found to consist

of a mixture of two solid fats, one resembling the margarine of olive-oil, and the other having a much higher melting-point, and other properties which distinguish it from that substance; it is called *stearine*.

These remarks apply to all ordinary oils and fats; it is by no means proved that the oleine and margarine of all vegetable and animal oils are identical; it is very possible that there may be essential differences among them, more especially in the case of the first-named substance.

Fixed fatty bodies, in contact with alkaline solutions at a high temperature, undergo the remarkable change termed *saponification*. When stearine, margarine, or oleine are boiled with a strong solution of caustic potash or soda, they gradually combine with the alkali, and form a homogeneous, viscid, transparent mass, or *soap*, freely soluble in warm water. If the soap so produced be afterwards decomposed by the addition of an acid, the fat which separates is found completely changed in character; it has acquired a strong acid reaction when applied in a melted state to test-paper, and it has become soluble with the greatest facility in warm alcohol; it is in fact a new substance, a true *acid*, capable of forming salts, and a compound ether, and has been generated out of the elements of the neutral fat under the influence of the base. Stearine, when thus treated, yields *stearic acid*, margarine gives *margaric acid*, oleine gives *oleic acid*, and common animal fat, which is a mixture of the three neutral bodies, affords by saponification by an alkali and subsequent decomposition of the soap, a mixture of the three fatty acids in question. These bodies are not, however, the only products of saponification; the change is always accompanied by the formation of a very peculiar sweet substance, called *glycerine*, which remains in the mother-liquor from which the acidified fat has been separated. The process of saponification itself proceeds with perfect facility in a close vessel; no gas is disengaged; the neutral fat, of whatsoever kind, is simply resolved into an alkaline salt of the fatty acid, or soap, and into glycerine.

STEARINE AND STEARIC ACID.—Pure stearine is most easily obtained by mixing purified mutton-fat, melted in a glass flask, with several times its weight of ether, and suffering the whole to cool. Stearine crystallizes out, while margarine and oleine remain in solution. The soft pasty mass may then be transferred to a cloth, strongly pressed, and the solid portion still further purified by recrystallization from ether. It is a white, friable substance, insoluble in water, and nearly so in cold alcohol; boiling spirit takes up a small quantity. Boiling ether dissolves it with great ease, but when cold, retains only $\frac{1}{225}$th of its weight.* The melting-point of pure stearine, which is one of its most important physical characters, may be placed at about 130° F.

When stearine is saponified, it yields, as already stated, glycerine and stearic acid. The latter crystallizes from hot alcohol in milk-white needles, which are inodorous, tasteless, and quite insoluble in water. It dissolves in its own weight of cold alcohol, and in all proportions at a boiling-heat; it is likewise soluble in ether. Alkaline carbonates are decomposed by stearic acid. Exposed to heat, it fuses, and at a higher temperature, if air be excluded, volatilizes unchanged. The melting-point of stearic acid is about 158°.

MARGARINE AND MARGARIC ACID.—The ethereal mother-liquor from which stearine has separated in the process just described, yields on evaporation, a soft-solid mixture of margarine and oleine with a little stearine. By compression between folds of blotting-paper, and re-solution in ether, it is rendered tolerably pure. In this state, margarine very much resembles stearine; it is, however, more fusible, melting at 116°, and very much more soluble in

* Lecanu, Ann. Chim. et Phys., lix. p. 195.

cold ether. By saponification it yields glycerine and margaric acid. The properties of this last-named substance resemble in the closest manner those of stearic acid; it is different in composition, however, more soluble in cold spirit, and has a lower melting-point, viz. 140°, or thereabouts. Its salts also resemble those of stearic acid.

A more or less impure mixture of stearic and margaric acids is now very extensively used as a substitute for wax and spermaceti in the manufacture of candles. It is prepared by saponifying tallow by lime, decomposing the insoluble soap so formed by boiling with dilute sulphuric acid, and then pressing out the fluid or oily portion from the acidified fat.

The solid part of olive-oil is said to be a definite compound of true margarine and oleine, inasmuch as its melting-point, 68°, is constant, and it gives by saponification a mixture of margaric and oleic acids.

Oleine and oleic acid.—It is doubtful whether a perfectly pure oleine has yet been obtained; the separation of the last portions of margarine, with which it is always naturally associated, is a task of extreme difficulty. Any fluid oil, animal or vegetable, which has been carefully decolorized, and filtered at a temperature approaching the freezing-point of water, may be taken as a representative of the substance. Oleic acid much resembles oleine in physical characters, being colorless, and lighter than water, but it has a distinct acid reaction, a sharp taste, and is miscible with alcohol in all proportions.

When stearic or margaric acid, or ordinary animal fats, are exposed to destructive distillation, they yield margaric acid, a new fatty body incapable of saponification, termed *margarone*, a liquid carburet of hydrogen, and various permanent gases. The neutral fats furnish besides an extremely pungent and even poisonous, volatile principle, called *acroleine*,* which has not yet been isolated.

In the manufacture of ordinary soaps, both potash and soda are used; the former yielding *soft*, and the latter *hard* soaps. Animal and vegetable fats are employed indifferently, and sometimes resin is added.

Composition of the preceding substances:—The following are the formulæ assigned by Liebig to the fatty acids; they are chiefly founded on investigations recently made at Giessen.†

Stearic acid, anhydrous	$C_{68}H_{66}O_5$
Margaric acid, anhydrous	$C_{68}H_{66}O_6$.

Margaric is thus seen to differ from stearic acid in containing an additional eq. of oxygen, and stearic acid can actually be converted into margaric by the action of oxidizing agents. Both are bibasic, and in their free or crystallized state contain 2 eq. of water.

Oleic acid from almond oil and beef-suet gave results agreeing pretty well, and leading to the following formula:

Oleic acid, anhydrous and monobasic,—$C_{44}H_{39}O_4$.

* *Acroleine* has been obtained by M. Redtenbacher, by distilling glycerine with anhydrous phosphoric acid. It is described as a colorless, limpid liquid, emitting a vapor very irritating to the eyes and organs of respiration. It is lighter than water, in which it is soluble, requiring about 20 parts, and forms a solution which is at first neutral, but soon becomes acid. It is more freely soluble in ether. It cannot be preserved without alteration, but is gradually converted into formic and acetic acids, and a new acid to which the name of acrylic acid has been given, while at the same time there is deposited a white flocculent matter, insoluble in water. The composition of acroleine is $C_6H_4O_2$, or glycerine, less four equivalents of the elements of water.—Revue Scientif., t. xvi. —R. B.

† See Annalen der Chemie und Pharmacie, xxxv. pp. 40, 65, 196.

Margarone probably contains $C_{66}H_{66}O_2$, or margaric acid *minus* 2 eq. of carbonic acid.

The composition of stearine, margarine and oleine is most safely deduced from a comparison of that of the acids to which they give rise, and of glycerine.

Margaric, stearic, and oleic acids have many properties in common; their salts much resemble each other, those of the alkalis being soluble in pure water when warm, but not in saline solutions. A large quantity of cold water added to an alkaline margarate or stearate occasions the separation of a crystalline, insoluble acid or super-salt. The margarates, stearates, and oleates of *lime*, *baryta*, and the oxides of the metals proper are insoluble in water. They are easily obtained by double decomposition, and in some few cases by direct action on the neutral fat. A solution of soap in alcohol is sometimes used as a test for the presence of lime, &c., in waters under examination.

Glycerine.—This substance is very readily obtained by heating together olive or other suitable oil, oxide of lead, and water, as in the manufacture of common *lead-plaster;* an insoluble soap of lead is formed, while the glycerine remains in the aqueous liquid. The latter is treated with sulphuretted hydrogen, digested with animal charcoal, filtered, and evaporated in vacuo at the temperature of the air. In a pure state, glycerine forms a nearly colorless and very viscid liquid, of sp. gr. 1·27, which cannot be made to crystallize. It has an intensely sweet taste, and mixes with water in all proportions; its solution does not ferment. Exposed to heat, it volatilizes in part, darkens, and becomes destroyed. Nitric acid converts it into oxalic acid.

Glycerine is composed of $C_6H_8O_6$.

Glycerine combines with the elements of sulphuric acid, forming a compound acid, the *sulphoglyceric*, $C_6H_7O_5$, $2SO_3$, which gives soluble salts with *lime*, *baryta*, and *oxide of lead.*

Palm and cocoa-oils.—These substances, which at the common temperature of the air have a soft-solid or buttery consistence, are now largely consumed in this country. *Palm oil* is the produce of the *elais guianensis*, and comes chiefly from the coast of Africa. It has, when fresh, a deep orange-red tint, and a very agreeable odor; the coloring matter, the nature of which is unknown, is easily destroyed by exposure to light, especially at a high temperature, and also by oxidizing agents. The oil melts at 80° F. By cautious pressure it may be separated into a fluid oleine and a solid substance, *palmitine*, which when purified by crystallization from hot ether, is perfectly white, fusible at 118°, soluble to a small extent only in boiling alcohol, and convertible by saponification into *palmitic acid.* The latter resembles in the closest manner margaric acid, and has the same melting-point; it differs in composition, however, containing $C_{32}H_{31}O_3$. By keeping, palm oil seems to suffer a change similar to that produced by saponification; in this state it is found to contain traces of glycerine, and a considerable quantity of oleic acid, together with a solid fatty acid, first supposed to be margaric, but which is probably palmitic acid. The oil becomes harder and rancid, and its melting-point is raised at the same time. Cocoa-oil, extracted from the kernel of the common cocoa-nut, is white, and has a far less agreeable smell than the preceding. It contains oleine and a solid fat, often used as a substitute for tallow in making candles, which, by saponification, gives a crystallizable fatty acid, *cocinic acid*, having the usual properties of these bodies, and melting at 95°. It is composed of $C_{27}H_{26}O_3$. Both this and palmitic acid are monobasic.

The solid vegetable fat from the *myristica moschata* contains a volatile oil, a fluid oleine, and a solid crystallizable, fatty principle; this, when saponified,

which occurs with difficulty, yields *myristic acid*. This substance melts at 120°, and contains $C_{28}H_{27}O_3$. It is monobasic.*

Elaidine and elaidic acid.—When olive-oil is mixed with a small quantity of nitrous acid, nitric acid containing that substance, or solution of nitrate of mercury made in the cold, it becomes after a few hours, a yellowish, soft-solid mass, which, pressed and treated with alcohol, furnishes a peculiar white, crystalline, fatty substance, termed *elaidine*. It resembles a neutral fat in properties, melts at 90°, dissolves with difficulty in boiling alcohol, easily in ether, and is resolved by saponification into glycerine and *elaidic acid*, which much resembles margaric acid. Oleic acid is directly convertible by nitrous acid into elaidic acid. It is not every kind of oil which furnishes elaidine; the drying oils, as those of linseed, poppy-seed, walnuts, &c., refuse to solidify; almond, olive and castor oils possess the property in a high degree.

Elaidic acid is said to contain $C_{72}H_{66}O_5$.

Suberic, succinic and sebacic acids.—*Suberic* acid has long been known as a product of the oxidation of *cork* by nitric acid; *succinic acid* is obtained by the distillation of amber; a fossil resin. Recently, both have been produced by the long-continued action of nitric acid upon stearic and margaric acids. Suberic acid is a white, crystalline powder, sparingly soluble in cold water, fusible and volatile by heat; it contains $C_8H_6O_3$. Succinic acid forms regular, colorless crystals, soluble in 5 parts of cold, and in half that quantity of boiling water; it is also fusible and volatile without decomposition, and contains $C_4H_2O_3$. *Sebacic* acid is a constant product of the destructive distillation of oleic acid, oleine, and all fatty substances containing those bodies; it is extracted by boiling the distilled matter with water. It forms small, pearly crystals resembling those of benzoic acid. It has a faint acid taste, is but little soluble in cold water, melts when heated, and sublimes unchanged. Sebacic acid is composed of $C_{10}H_8H_3$.

Butyrine; butyric acid.—Common butter chiefly consists of a solid, crystallizable and easily fusible fat, a fluid oily substance, and a yellow coloring matter, besides mechanical impurities, as caseine. The oily part appears to be a mixture of oleine and a peculiar odoriferous fatty principle, *butyrine*, not yet isolated, which by saponification yields three distinct volatile acids, the *butyric*, the *capric*, the *caproic*, easily separable in virtue of the very unequal solubility of their baryta-salts. Butyric acid is a colorless, oily liquid, of sour taste, and an odor resembling old and rancid butter, in which it is probably present. It has a density of ·976, dissolves in all proportions in water, acids, alcohol, ether, and oils, and readily distils without decomposition. Capric and caproic acids greatly resemble butyric in properties, but are less soluble in water. A very similar substance, *phocenic* acid, is procured by the saponification of fish or whale oil, and is derived without doubt from a corresponding neutral fatty principle.

Butyric acid has very recently acquired a certain degree of importance from the curious discovery of M. Pelouze, that sugar, under particular circumstances, is susceptible of becoming converted into that substance. A tolerably strong solution of common sugar mixed with a small quantity of caseine and some chalk, and exposed for some time to a temperature of 80° or a little higher, yields by a species of fermentation, in which the caseine is the active *ferment*, a large amount of butyrate of lime; carbonic acid and hydrogen gases are during the whole period extricated. This is an exceedingly interesting case of the half-artificial formation of an animal product.†

Butyric acid contains, according to Pelouze, $C_8H_7O_3$.

* Annalen der Chemie und Pharmacie, xxxv. p. 277; xxxvi. p. 50; xxxvii. p. 152; also, Liebig in Geiger's Pharmacie; or, Turner's Chemistry, edited by Dr. Gregory.

† Annalen der Chemie und Pharmacie, xlvii. p. 241.

Wax.—Common bees-wax, freed from its yellow coloring matter by bleaching, may be separated by boiling alcohol into two different proximate principles, *cerine* and *merycine*. The first is a white crystalline substance, soluble in about 16 parts of boiling spirit, and melting at 144°; it is the most abundant of the two. The second is very much less soluble in alcohol, and rather less fusible. It is much to be questioned whether these bodies are susceptible of saponification.

Spermaceti.—The soft-solid matter, found in very large quantity in a remarkable cavity or chamber in the head of the spermaceti whale, when submitted to pressure yields, as is well known, a most valuable fluid oil, and a crystalline, brownish substance, which, when purified, becomes the beautiful snow-white article of commerce, spermaceti. This substance appears, by the most recent experiments, to be a specific neutral fatty body, and not, as formerly supposed, a mixture of several proximate principles.* It melts at 120°, and when cooled under favorable circumstances, forms distinct crystals. Boiling alcohol dissolves it in small quantity, and ether in much larger proportion. Spermaceti is saponified with great difficulty; two products are obtained, *ethal* and *ethalic acid;* the first is a natural, crystallizable fat, whose melting-point is nearly the same as that of spermaceti itself, but its solubility in alcohol is much greater; it is also readily sublimed without decomposition. Ethalic acid resembles in many respects margaric acid.

Spermaceti is composed of $C_{64}H_{64}O_4$.

Cholesterine.—This substance is found in small quantity in various parts of the animal system, as in the bile, in the brain and nerves, and in the blood; it forms the chief ingredient of *biliary calculi*, from which it is easily extracted by boiling the powdered gall-stones in strong alcohol, and filtering the solution while hot; on cooling, the cholesterine crystallizes in brilliant, colorless plates. It has the characters of a fat, is insoluble in water, tasteless and inodorous; it is freely soluble in boiling spirit, and also in ether. It altogether resists saponification. Cholesterine melts at 278°, and contains probably $C_{36}H_{32}O$.

Cantharidine, the active principle of the Spanish fly, may be here mentioned. It is a colorless crystallizable, fatty body, extracted by ether or alcohol from the insect; it is insoluble in water and dilute acids, and volatile when strongly heated. The vapor attacks the eyes in a very painful manner. Cantharidine contains $C_{10}H_6O_4$.†

VOLATILE OILS.

The volatile oils of the vegetable kingdom are exceedingly numerous; they are secreted by plants, and confer upon their flowers, fruits, leaves, and wood, their peculiar odors. These substances are mostly procured by distilling the plant, or part of the plant, with water; their points of ebullition always lie above that of water; nevertheless, at 212° the oils emit vapor of very considerable tension, which is carried over mechanically, and condensed with the steam. The milky, or turbid liquid obtained, when left to rest, separates into oil and water. Sometimes the oil is heavier than the water, and sinks to the bottom; sometimes the reverse happens.

The volatile oils, when pure, are colorless; they very frequently, however, have a yellow, and in rarer cases, a green color, from the presence of impurity. The odor of these substances is usually powerful, and their taste pungent

* L. Smith, Idem. xlii. p. 241.

† We are indebted to M. Chevreul for the first series of scientific researches on the fixed oils and fats, and on the theory of saponification. These admirable investigations are detailed in the early volumes of the Annales de Chimie et de Physique, and were afterwards published in a separate form in 1823, under the title of "Recherches chimiques sur les corps gras d'origine animale."

and burning. They resist saponification completely, but when exposed to the air frequently become altered by slow absorption of oxygen, and assume the character of resins. They mix in all proportions with fat oils, and dissolve freely both in ether and alcohol; from the latter solvent they are precipitated by an addition of water. As already mentioned, the volatile oils communicate a greasy stain to paper, which disappears by warming; by this character any adulteration with fixed oil can be at once detected. A solid, crystalline matter, corresponding to the margarine of the common oils, frequently separates from these bodies; it bears the general name of *stearopten*, and differs probably in almost every case.

The essential oils may be conveniently divided into three classes: viz., those consisting of carbon and hydrogen only; those consisting of carbon, hydrogen, and oxygen; and those containing in addition sulphur and nitrogen.

Oils composed of carbon and hydrogen. Oil, or essence of turpentine.—This substance may be taken as the type or representative of the class; it is obtained by distilling with water the soft, or semi-fluid balsam, called in commerce *crude turpentine*, which exudes from various pines and firs, or flows from wounds made for the purpose in the wood. The solid product left after distillation, is common resin. Oil of turpentine, when further purified by rectification, is a thin, colorless liquid of powerful and well-known odor; its density in the liquid state is ·865, and that of its vapor 4·764; it boils at 312°. In water it dissolves to a small extent, and in strong alcohol and ether much more freely; with fixed oils it mixes in all proportions. Strong sulphuric acid chars and blackens this substance; concentrated nitric acid and chlorine attack it with such violence that inflammation sometimes ensues.

Oil of turpentine is composed of C_5H_4.

With hydrochloric acid the oil forms a curious compound, which has been called *artificial camphor* from its resemblance in odor and appearance to that substance. It is prepared by passing dry hydrochloric acid gas into the pure oil, cooled by a freezing mixture. After some time, a white crystalline substance separates, which may be strained from the supernatant brown and highly acid liquid, and purified by alcohol, in which it dissolves very freely. This substance is neutral to test-paper, does not affect nitrate of silver, and sublimes without much decomposition; it contains $C_{20}H_{17}Cl$, or, perhaps, $C_{20}H_{16}$, HCl. The dark mother-liquor contains a somewhat similar, but fluid compound. Different specimens of oil of turpentine yield very variable quantities of these substances, which may, perhaps, arise from the co-existence of *two* very similar and isomeric oils in the ordinary article. Oil of turpentine is very largely used in the arts in painting, and as a solvent for resins in making varnishes.

Oil of lemons is expressed from the rind of the fruit, or obtained by distillation with water. This oil differs very much from the last in odor, but closely resembles it in other respects. It has the same composition as oil of turpentine, and forms, with hydrochloric acid, two compounds, one solid and crystalline, the other fluid. The solid contains $C_{10}H_8$, HCl. The oils of *copaiba-balsam*, *juniper-berries*, *storax*, and several others, contain no oxygen.

Essential oils containing oxygen.—These are very numerous; two of the most interesting, bitter-almond and cinnamon-oil, have been already described, and may be considered typical of the rest. Among the others may be mentioned the oils of *roses*, *bergamot*, *peppermint*, and other allied species, *lavender*, and *cajeput*. All these have been yet but imperfectly examined. *Common camphor* is a solid oil, or volatile fat, of this class; it partakes of the general properties of the volatile oils, being vaporizable without change at a moderate heat, nearly insoluble in water, and soluble with facility in spirit.

It is composed of $C_{10}H_8O$. By oxidation by nitric acid, camphor yields *camphoric acid*, which contains $C_{10}H_7O_3$, and somewhat resembles in properties benzoic acid.

ESSENTIAL OILS CONTAINING SULPHUR.—The most remarkable member of this class is the oil obtained by distillation from black mustard-seed. White mustard yields none. Both varieties give, by expression, a bland, fat oil. The volatile oil does not pre-exist in the seed, but is formed in the same manner as bitter-almond oil, by the joint action of water, and a peculiar coagulable albuminous matter, upon a substance yet imperfectly known, present in the grain, and termed *myronic acid.*

The distilled oil, when pure, is colorless; it has a most powerful and suffocating smell, and a density of 1·015. It boils at 289°. Water dissolves it in small quantity, and alcohol and ether very freely. The oil itself, at a high temperature, dissolves both sulphur and phosphorus, and deposits them in a crystalline form on cooling. It is oxidized with violence by nitric acid, and by aqua regia. Alkalis decompose it by the aid of heat, with production of ammonia, an alkaline sulphuret, and a sulphocyanide. Mustard-oil gives by analysis $C_{32}H_{20}N_4S_5O_5$.

With ammonia, this substance forms a very extraordinary compound, which crystallizes in colorless, rhombic prisms, easily soluble in hot water, alcohol, and ether. The solution is quite neutral, and is not precipitated by any of the ordinary re-agents. When mixed with solution of fixed alkali, it exhales no ammonia; neither can the oil be again obtained from it by any known means. The ultimate composition of this curious body is expressed by the formula $C_{32}H_{32}N_8S_5O_5$, which contains the elements of mustard-oil, and 4 eq. of ammonia.

The oils of *horseradish*, *onions*, *assafœtida*, and *hops*, contain sulphur, and consequently belong to the same series; they have not yet been thoroughly examined.

RESINS AND BALSAMS.

Common resin, or *colophony*, furnishes perhaps the best example of the class. The origin of this substance has been already described. It is a mixture of two distinct bodies, having acid properties, called *pinic* and *sylvic acids*, separable from each other by their difference of solubility in cold and somewhat dilute alcohol, the former being by far the most soluble of the two. Pure sylvic acid crystallizes in small, colorless, rhombic prisms, insoluble in water, soluble in hot, strong alcohol, in volatile oils, and in ether. It melts when heated, but cannot be distilled without decomposition. The properties of pinic acid are very similar. Both have the same composition, viz., $C_{20}H_{15}O_2$. A third resin-acid, also isomeric with the preceding, the *pimaric*, has been found in the turpentine of the *pinus maritima* of Bordeaux.

Lac is a very valuable resin, much harder than colophony, and easily soluble in alcohol; three varieties are known in commerce, viz., *stick-lac*, *seed-lac*, and *shellac*. It is used in varnishes, and in the manufacture of hats, and very largely in the preparation of sealing-wax, of which it forms the chief ingredient. Crude lac contains a red dye, which is partly soluble in water. Lac dissolves in considerable quantity in a hot solution of borax; Indian ink, rubbed up with this liquid, forms a most excellent *label-ink* for the laboratory, as it is unaffected by acid vapors, and, when once dry, becomes nearly insoluble in water.

Mastic, *Dammar-resin*, and *sandaric* are resins largely used by the varnish-maker. *Dragon's blood* is a resin of a deep-red color. *Copal* is also a very valuable substance; it differs from the other resins in being with difficulty

dissolved by alcohol and essential oils. It is miscible, however, in the melted state with oils, and is thus made into varnish. *Amber* appears to be a fossil resin; it is found accompanying brown-coal or lignite.

CAOUTCHOUC.—This curious, and now most useful substance, is the produce of several trees of tropical countries, which yield a milky juice, hardening by exposure to the air. In a pure state, it is nearly white, the dark color of commercial caoutchouc being due to the effects of smoke, and other impurities Its physical characters are well known. It is softened, but not dissolved by boiling water; it is also insoluble in alcohol. In pure ether, rectified native naphtha, and coal-oil, it dissolves, and is left unchanged on the evaporation of the solvent. Oil of turpentine also dissolves it, forming a viscid, adhesive mass, which dries very imperfectly. At a temperature a little above the boiling-point of water, caoutchouc melts, but never afterwards returns to its former elastic state. Few chemical agents affect this substance; hence its great practical use, in chemical investigations, for connecting apparatus, &c. Analysis shows it to contain nothing but carbon and hydrogen.

Most of the resins, when exposed to destructive distillation, yield liquid, oily pyro-products, usually carburets of hydrogen, which have been studied with partial success. Great difficulties occur in these investigations; the task of separating from each other, and isolating bodies which scarcely differ but in their boiling-points, is exceedingly troublesome.

Balsams are also, as before hinted, natural mixtures of resins with volatile oils. These differ very greatly in consistence, some being quite fluid, others solid and brittle. By keeping, the softer kinds often become hard. Balsams may be conveniently divided into two classes, viz., those which, like *common* and *Venice turpentine*, *Canada balsam*, *copaiba balsam*, &c., are merely natural varnishes, or solutions of resins in volatile oils, and those which contain benzoic or cinnamic acid in addition, as *Peru* and *Tolu balsams*, and the solid resinous *benzoin*, commonly called *gum-benzoin*.

SECTION VIII.

COMPONENTS OF THE ANIMAL BODY.

ALBUMINOUS, OR PROTEINE GIVING PRINCIPLES. ALBUMEN.—The fluid portion of blood which has been some time drawn from the living body, and the white of eggs, contain this substance as their chief and characteristic ingredient; it is in both cases associated with certain inorganic salts, and a small quantity of free soda, to which these liquids owe their alkaline reaction. In the purest form in which albumen has yet been obtained it is insoluble, or nearly so, in water. If clear serum of blood, or white of egg mixed with a little water and filtered, be exactly neutralized by acetic acid, and then largely diluted with pure cold water, a copious flocculent precipitate falls, which may be collected on a filter, and washed. In this state it is nearly colorless, inodorous, and tasteless; it dissolves with facility in water containing an exceedingly small quantity of caustic alkali, and gives a solution which has all the characters of the original liquid. When dried by gentle heat, it shrinks to a very small bulk and becomes a translucent, horny mass, which softens in water, and exhales when exposed to heat, the usual ammoniacal products of animal matter, leaving a bulky coal, very difficult of combustion. When white of egg is thinly spread upon a plate and exposed to evaporation in a warm place, it dries up to a pale yellow, brilliant, gum-like substance, destitute of all traces of crystalline structure. In this state it may be preserved unchanged for any length of time, the presence of water being in all cases necessary to putrefactive decomposition. The dried white of egg may also be exposed to a heat of 212° without alteration of properties. When put into slightly warm water, it softens, and at length in great measure dissolves. When reduced to fine powder and washed upon a filter with cold water, common salt, sulphate, phosphate, and carbonate of soda are dissolved out, together with mere traces of organic matter, while a soft, swollen mass remains upon the filter, which has all the characters of pure albumen obtained by precipitation. When dried and incinerated, this leaves nothing but a little phosphate of lime.

It thus appears likely that albumen is really an insoluble substance, and that its soluble state in the animal system is due to the presence of a little alkali.

When natural albumen is exposed to heat it solidifies, or *coagulates*. The temperature required for this purpose varies with the state of dilution. If the quantity of albumen be so great that the liquid has a slimy aspect, a heat of 145° or 150° suffices, and the whole becomes solid, white and opaque; in a very dilute condition, boiling is required, and the albumen then separates in light, finely-divided flocks. Thus changed by heat, albumen becomes quite insoluble in water; it dries up to a yellow, transparent, horny substance, which when macerated in water, resumes its former whiteness and opacity. In dilute caustic alkali it dissolves with facility, and in this respect resembles the *insoluble* albumen just described; it differs, however, from the latter in not being soluble in a strong solution of nitrate of potash, which dissolves with great ease that substance. The only chemical change that can be traced in the act

of coagulation is the loss of alkali and soluble salts, which are removed by the hot water.

A solution of ordinary albumen gives precipitates with excess of sulphuric, hydrochloric, nitric, and *meta*phosphoric acids; but neither with acetic nor with common or tribasic phosphoric acid; both these acids having the property of dissolving pure albumen. These precipitates are looked upon as direct compounds of albumen with the acids in question. Most of the metallic salts, as those of copper, lead, mercury, &c., form insoluble compounds with albumen, and give precipitates with its solution; hence the value of white of egg as an antidote in cases of poisoning with corrosive sublimate. Alcohol, added in large quantity, precipitates albumen. Tannic acid, or infusion of galls, gives with it a copious precipitate. By these characters the presence of albumen may be readily discovered, and its identification effected; a *very* feebly alkaline liquid, if containing albumen, coagulates by heat, becomes turbid on the addition of nitric acid, and, previously acidulated by acetic acid, gives a precipitate with solution of corrosive sublimate. It must be remembered, that a considerable quantity of alkali prevents coagulation by heat, and the addition of acetic acid, indispensable to the mercury-test, produces the same effect.

The chemical composition of albumen has been carefully studied; it contains in 100 parts—*

Carbon	54·84
Hydrogen	7·09
Nitrogen	15·83
Oxygen	21·23
Phosphorus	·33
Sulphur	·68
	100·

From this the highly complex formula $C_{400}H_{310}N_{50}O_{120}PS_2$ is deducible.

The existence of unoxidized sulphur in albumen is easily shown; a boiled egg blackens a silver spoon from a trace of alkaline sulphuret formed or separated during the coagulation; and a solution of albumen in excess of caustic potash, mixed with a little acetate of lead, gives on boiling a black precipitate containing sulphuret of lead.

FIBRINE.—This substance is found in the animal body in two distinct states, viz. in the solid form, in muscular fibre, and in solution, in the blood. A thin slice of muscular flesh washed in cold water until perfectly white affords an example of impure fibrine in the state first-mentioned, associated, however, with membranous matter, nerves and fat. It is procured in a far purer condition by washing the coagulum of blood in a cloth until all the soluble portions are removed, or by agitating fresh blood with a bundle of twigs, when the fibrine attaches itself to the latter, and is easily removed and cleansed by repeated washing with cold water. The only then remaining impurity is a small quantity of fat which can be extracted by ether. In the fresh state fibrine forms long, white, elastic filaments, which under the microscope appear to be composed of small globules arranged in strings; it is quite tasteless, and insoluble in both hot and cold water. By long-continued boiling it is partly dissolved. When dried in vacuo, or at a gentle heat, it loses about 80 per cent. of water, and becomes translucent and horny; in this state it closely resembles coagulated albumen. Fresh fibrine wetted with concentrated acetic acid, forms, after some hours, a transparent jelly, which slowly dissolves in pure water; put into very dilute caustic alkali, fibrine dissolves completely, and the

* Mulder, quoted by Berzelius, Lehrbuch, ix. p. 47.

solution exhibits many of the characters of albumen. Phosphoric acid produces a similar effect.

The fibrine of arterial and venous blood is not absolutely the same; when the venous fibrine of human blood is triturated in a mortar with 1½ times its weight of water and ⅙ of its weight of nitrate of potash, and the mixture left 24 hours or more at a temperature of 100°—120°, it becomes gelatinous, slimy, and eventually entirely liquid; in this condition it exhibits all the properties of a solution of albumen which has been neutralized by acetic acid. It coagulates by heat, it is precipitated by alcohol, corrosive sublimate, &c., and when largely diluted it deposits a flocculent substance, not to be distinguished from insoluble albumen.* With arterial fibrine, on the contrary, no such liquefaction happens, and even the fibrine of venous blood, when long exposed to the air, or to oxygen gas, loses the property in question. The fibrine of muscular flesh resembles that of venous blood.

In the soluble state, fibrine is in great measure unknown; when withdrawn from the influence of life, it coagulates spontaneously after a certain interval, giving rise to the production of the clot which appears in blood left to itself, and which consists of a kind of fine net-work of fibres, swollen with liquid serum, and enclosing the little red coloring particles of the blood, hereafter to be described.

M. Mulder found dried fibrine, carefully freed from fat, to be composed as follows:—

Carbon	54·56
Hydrogen	6·90
Nitrogen	15·72
Oxygen	22·13
Phosphorus	·33
Sulphur	·36
	100·

The formula, $C_{400}H_{310}N_{50}O_{120}PS$, agrees with this result perfectly well.

The ash, or incombustible portion of fibrine, varying from ·7 to 2·5 per cent., consists chiefly of the phosphates of lime and magnesia.

Caseine.—This is the characteristic azotized component of milk, and the basis of the various preparations termed cheese; it is not known to occur in any other secretion. Caseine very closely resembles albumen in many particulars, and may even be occasionally confounded with it. Like that substance, it is insoluble in water when in a state of purity, and only assumes the soluble condition in the presence of free alkali, of which, however, a very small quantity suffices for the purpose.† To prepare caseine, fresh milk is gently warmed with dilute sulphuric acid, the coagulum produced well washed with water, dissolved in dilute solution of carbonate of soda, and placed in a warm situation to allow the fat or butter to separate from the watery liquid. The latter is then removed by a siphon, and re-precipitated by sulphuric acid. These precipitations and re-solutions in dilute alkali are several times repeated. Lastly, the insoluble caseine is well washed with boiling water, and treated with ether to remove the last traces of fat. In this state it is a white curdy substance, not sensibly soluble in pure water or in alcohol, but dissolved with great ease by water containing a little caustic or carbonated alkali. It is also soluble to a certain extent in dilute acids, from which it may be precipitated by cautious neutralization. The precipitate formed by an acid in a strong

* Liebig, Handwörterbuch der Chemie, i. p. 881.
† Rochleder, Annalen der Chemie und Pharmacie, xlv. p. 253.

solution of caseine contains acid in combination, which, however, may be entirely removed by washing. In the moist state caseine reddens litmus paper, and masks the reaction of an alkaline carbonate. When incinerated, it leaves about ·3 per cent. of incombustible matter.

A solution of caseine in very dilute alkali, as in milk, does not coagulate on boiling; hence it is easily distinguished from albumen. On evaporation the surface becomes covered by a skin, and the whole eventually dries up to a translucent mass. Acetic acid precipitates caseine, which is another distinctive character between that substance and albumen.

The most striking property of caseine is its coagulability by certain animal membranes. This is well seen in the process of cheese-making, in the preparation of the *curd*. A piece of the stomach of the calf, with its mucous membrane, is slightly washed, put into a large quantity of milk, and the whole slowly heated to about 122°. In a short time after this temperature has been attained, the milk is observed to separate into a solid, white coagulum, or mass of curd, and into a yellowish, translucent liquid called *whey*. The curd contains all the caseine of the milk, much of the fat, and much of the inorganic matter; the whey retains the milk-sugar and the soluble salts. It is just possible that this mysterious change may be really due to the formation of a little lactic acid from the milk-sugar, under the joint influence of the slowly decomposing membrane, and the elevated temperature, and that this acid may be sufficient in quantity to withdraw the alkali which holds the caseine in solution, and thus occasion its precipitation in the insoluble state. The loss of weight the membrane itself suffers in this operation is very small; it has been found not to exceed $\frac{1}{1800}$ part.

Caseine has been carefully analyzed by Mulder; it contains in 100 parts,

Carbon	54·96
Hydrogen	7·15
Nitrogen	15·80
Oxygen	21·73
Sulphur	·36
	100·

The formula, $C_{400}H_{310}N_{50}O_{120}S$, agrees very closely with these numbers.

A comparison of the composition of the three bodies described will enable the student at once to trace their curious and highly interesting chemical relations. The first two contain, as essential components, both phosphorus and sulphur, the proportions of which, small as they are, differ. The last contains no phosphorus, but sulphur only. So far, however, as regards the carbon, hydrogen, oxygen, and nitrogen, *the three substances are in composition identical.*

PROTEINE.—When albumen, fibrine, or caseine is dissolved in a moderately strong solution of caustic alkali, filtered, and mixed with a slight excess of acid, a copious, snow-white, flocculent precipitate falls and a faint odor of sulphuretted hydrogen is evolved. The new substance is proteine;* it may be placed upon a filter, washed, dried and examined. It is tasteless and insoluble, and much resembles caseine in properties, but is soluble in acetic acid. Dilute alkali dissolves it with great ease. It is quite indifferent which of the three albuminous principles be employed in the preparation of proteine; the result is the same.

Proteine is found on analysis to contain the four organic elements, in the

* So called from πρωτεύω, I take the first place; in allusion to its important relations to the albuminous principles.

proportions in which they exist in albumen, fibrine, and caseine, and nothing besides. 100 parts yield,

	From albumen.	From fibrine.	From caseine.
Carbon	55·30	55·44	55·16
Hydrogen	6·94	6·95	7·17
Nitrogen	16·02	16·05	15·86
Oxygen	21·74	21·56	21·81
	100.	100·	100·

These numbers lead directly to the *empirical* formula $C_{40}H_{31}N_5O_{12}$.

There are two methods of interpreting the appearance or production of this remarkable substance. It may be that it pre-exists in the three natural albuminous principles, which on that supposition may be viewed as compounds of proteine with sulphur and phosphorus, or with sulphur only; the probability may, on the other hand, be urged that proteine is merely a *product* of the action of alkalis on those bodies, the phosphorus and sulphur being at the same time separated, the first as phosphoric acid, and the second as sulphuret of the alkaline metal.

When proteine, or substances which yield it, are boiled in strong solution of potash as long as ammoniacal vapors are given off, the liquid then neutralized with sulphuric acid, evaporated to dryness, and the product exhausted by boiling alcohol, three compounds are dissolved out, viz., a soluble, brown extract-like substance, *erythroprotide;* a soluble straw-yellow substance, *protide*, and a curious crystallizable principle, *leucine*, which forms small colorless scales, destitute of taste and odor, soluble in water and alcohol, and in concentrated sulphuric acid without decomposition. When heated, it sublimes unchanged. Leucine contains $C_{12}H_{12}NO_4$.

Binoxide and tritoxide of proteine of Mulder.—These are products of the long-continued action of boiling water upon fibrine in contact with air; they are the chief ingredients also of the *buffy coat* of blood in a state of inflammation, being produced at the expense of the fibrine.* *Binoxide of proteine* is quite insoluble in water, but dissolves in dilute acids; when dry it is dark-colored. This substance is constant in composition, containing $C_{40}H_{31}N_5O_{14}$. The soluble part of the fibrine-decoction contains *tritoxide of proteine*, $C_{40}H_{31}N_5O_{15}+HO$, which somewhat resembles, and has been confounded with, gelatine. It is freely soluble in alcohol and in dilute alkalis. Coagulated albumen is slowly dissolved by boiling-water, and converted into this substance.

When chlorine gas is passed to saturation into a solution of ordinary albumen, or either fibrine or caseine dissolved in ammonia, a white, flocculent, insoluble substance falls, which, when washed and dried, becomes a soft, yellowish powder. This is supposed to be a compound of chlorous acid and proteine; when digested with ammonia, it yields sal-ammoniac and tritoxide of proteine.

Gelatine and chondrine.—Animal membranes, skin, tendons, and even bones, dissolve in water at high temperature more or less completely, but with very different degrees of facility, giving solutions which on cooling acquire a soft-solid, tremulous consistence. The substance so produced is termed *gelatine;* it does not pre-exist in the animal system, but is generated from the membranous tissue by the action of hot water. The jelly of calves' feet, and common size and glue, are familiar examples of gelatine in different conditions of purity. Isinglass, the dried swimming bladder of the sturgeon, dissolves in water merely warm, and yields a beautifully pure gelatine. In

* Mulder, Annalen der Chemie und Pharmacie, xlvii. p. 323.

this state it is white and opalescent, or translucent, quite insipid and inodorous, insoluble in cold water, but readily dissolved by a slight elevation of temperature. Cut into slices and exposed to a current of dry air, it shrinks prodigiously in volume, and becomes a transparent, glassy, brittle mass, which is soluble in warm water, but insoluble in alcohol and ether. Exposed to destructive distillation, it gives a large quantity of ammonia, inflammable gases, nauseous empyreumatic oil, and leaves a bulky charcoal containing nitrogen. In a dry state, gelatine may be kept indefinitely; in contact with water, it putrefies. Long-continued boiling gradually alters it, and the solution loses the power of forming a jelly on cooling. One part of dry gelatine or isinglass dissolved in 100 parts of water solidifies on cooling.

An aqueous solution of gelatine is precipitated by alcohol, which withdraws the water; corrosive sublimate in excess gives a white, flocculent precipitate, and the same happens with solution of nitrate of the sub- and protoxide of mercury; neither alum, acetate, nor sub-acetate of lead affect a solution of gelatine. With tannic acid or infusion of galls, gelatine gives a copious, whitish, curdy precipitate, which coheres on stirring to an elastic mass, quite insoluble in water, and incapable of putrefaction.

Chlorine passed into a solution of gelatine occasions a dense white precipitate of *chlorite of gelatine*, which envelops each gas-bubble, and ultimately forms a tough, elastic, pearly mass, somewhat resembling fibrine. Boiling with strong alkalis, converts gelatine, with evolution of ammonia, into leucine, and a sweet, crystallizable principle, *gelatine-sugar* (*glycicoll*), which contains $C_{16}H_{18}N_4O_{14}$.*

Dry gelatine, subjected to analysis, has been found to contain in 100 parts,

Carbon	50·05
Hydrogen	6·47
Nitrogen	18·35
Oxygen	25.13
	100·

From these numbers the formula $C_{13}H_{10}N_2O_5$ has been deduced. This stands in no obvious relation to that of the proteine-compounds.

The cartilage of the ribs and joints yields a gelatine differing in some respects from the preceding; it is called by way of distinction, *chondrine*. Acetate of lead and solution of alum precipitate this substance, which is not the case with common gelatine. Chondrine contains $C_{16}H_{13}N_2O_7$.

If a solution of gelatine, albumen, fibrine, caseine, or probably any one of the more complex azotized animal principles, be mixed with solution of sulphate of copper, and then a large excess of caustic potash added, the greenish precipitate first formed is re-dissolved, and the liquid acquires a purple tint of indescribable magnificence and great intensity.

Gelatine is largely employed as an article of food, as in soups, &c., but its value in this respect has been to a certain extent questioned. In the useful arts, size and glue are consumed in great quantities. These are prepared from the clippings of hides, and other similar matters, enclosed in a net, and boiled with water in a large caldron. The strained solution gelatinizes on cooling, and constitute *size*. Glue is the same substance in a state of desiccation, the size being cut into slices and placed upon netttings, freely exposed to a current of air. Gelatine is extracted from bones with much greater dif-

* According to Gerhardt glycicoll has the composition of $C_4H_5NO_4$. It unites with both acids and bases. The compounds formed with the acids are themselves acids, and combine with bases, giving rise to double salts. Gelatine sugar does not undergo fermentation. In its relations it bears more analogy to urea, than to any of the saccharine substances.—R.B.

ficulty; the best method of proceeding is said to be to enclose the bones, previously crushed in strong metallic cylinders, and admit high-pressure steam, which attacks and dissolves the animal matter much more easily than boiling water; or to steep the bones in dilute hydrochloric acid, thereby remove the earthy phosphate, and then dissolve the soft and flexible residue by boiling.

There is an important economical application of gelatine, or rather of the material which produces it, which deserves notice, viz., to the clarifying of wines and beer from the finely-divided suspended matter which often renders these liquors muddy and unsightly. When isinglass is digested in very dilute cold acetic acid, as sour wine or beer, it softens, swells, and assumes the aspect of a very light, transparent jelly, which although quite insoluble in the cold, may be readily mixed with a large quantity of watery liquid. Such a preparation, technically called *finings*, is used by the brewer and wine-merchant for the purpose before-mentioned; its action on the liquor with which it is mixed seems to be purely mechanical, the gelatinous matter slowly subsiding to the bottom of the cask, and carrying with it the insoluble substance to which the turbidity was due.

COMPOSITION OF THE BLOOD; RESPIRATION.—The blood is the general circulating fluid of the animal body, the source of all nutriment and growth, and the general material from which all the secretions, however much they may differ in properties and composition, are derived. Food or nourishment from without can only be made available by being first converted into blood. It serves also the scarcely less important office of removing and carrying off principles from the body which are hurtful, or no longer required.

In all vertebrated animals the blood has a red color, and probably in all cases a temperature above that of the medium in which the creature lives. In the mammalia this is very apparent, and in the birds still more so. The heat of the blood is directly connected with the degree of activity of the respiratory process. In man the temperature of the blood seldom varies much from 98° F., when in a state of health, even under great vicissitude of climate; in birds it is sometimes as high as 109°. To these two highest classes of the animal kingdom, the mammifers and the birds, the observations about to be made are intended especially to apply.

In every creature of this description, two kinds of blood are met with, which differ very considerably in their appearance, viz., that contained in the *left* side of the heart, and in the arteries generally, and that contained in the *right* side of the heart, and in the veins; the former, or *arterial* blood, has a bright-red color; the latter, the *venous* blood, is blackish purple. Further, the conversion of the dark into the florid blood may be traced to what takes place during its exposure to the air in the lungs, and the opposite change, to what takes place in the capillaries of the general vascular system, or the minute tubes or passages, distributed in countless numbers throughout the whole body, which connect the extremities of the arteries and veins. When compared together, little difference of properties or composition can be found in the two kinds of blood; the fibrine varies a little, that from venous blood being, as already mentioned, soluble in a solution of nitrate of potash, which is not the case with arterial fibrine. It is very prone, besides, to absorb oxygen, and to become in all probability partly changed to binoxide of proteine, which no doubt exists in the fibrine of arterial blood. The only other notable point of difference is the gaseous matter the blood holds in solution, carbonic acid predominating in the venous, and free oxygen in the arterial variety.

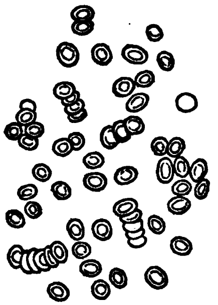
In its ordinary state the blood has a slimy feel, a density varying from 1·053 to 1·057, and a decidedly alkaline reaction; it has a saline and disagreeable taste, and when quite recent, a peculiar odor or *halitus*, which almost imme-

diately disappears. An odor may, however, afterwards be developed by an addition of sulphuric acid, which is by some considered characteristic of the animal from which the blood was obtained.

The coagulation of blood in repose has been already noticed, and its cause traced to the spontaneous solidification of the fibrine: the effect is best seen when the blood is received into a shallow vessel, and left to itself some time. No evolution of gas, or absorption of oxygen takes place in this process. By strong agitation, coagulation may be prevented; the fibrine in this case separates in cohering filaments.

To the naked eye the blood appears a homogeneous fluid, but it is not so in reality. When examined by a good microscope, it is seen to consist of a transparent and nearly colorless liquid, in which float about a countless multitude of little round red bodies, to which the color is due; these are the *blood-discs* or *blood-corpuscles* of microscopic observers. They are accompanied by a number of minute, colorless globules, some of which consist of fat, while the others are, perhaps, the matter of chyle.

Fig. 162.



The bodies in question are found to present different appearances in the blood of different animals: in the mammifers they look like little round red or yellowish discs, thin when compared with their diameter, and having in the centre either a depression, or a small colorless, transparent spherule or nucleus; it is not certain which. In birds, lizards, frogs, and fish, the corpuscles are elliptical. In magnitude, they seem to be pretty constant in all the members of a species, but differ with the genus and order. In man they are very small, varying form $\frac{1}{6000}$ to $\frac{1}{3000}$th of an inch in breadth, while in the frog the long diameter of the ellipse measures at least four times as much. The corpuscles consist essentially of the red coloring-matter of the blood.

The coagulation of blood effects a kind of natural proximate analysis; the clear, pale serum, or fluid part, is an alkaline solution of albumen, containing various soluble salts; the clot is a mechanical mixture of fibrine and coloring principle, swollen and distended with serum, of which it absorbs a large but variable quantity.

When the coagulum of blood is placed upon bibulous paper, and drained as much as possible from the fluid portion, and then put into water, the coloring matter dissolves, forming a magnificent crimson solution, which has many of the characters of a dye-stuff. It contains albumen, and coagulates by heat and by the addition of alcohol; this albumen cannot be separated, and all attempts to isolate the *hematosine* or red pigment have consequently failed. From its extreme susceptibility of change, nothing is known respecting it in a state of purity. The above watery solution, exposed with extensive surface in a warm place, dries up to a dark-red, brittle mass, which is again soluble in water. After coagulation, it becomes quite insoluble, but dissolves like albumen in caustic alkalis. Carbonic and sulphurous acids blacken the red solution; oxygen, or atmospheric air, heightens its color; protoxide of nitrogen renders it purple; while sulphuretted hydrogen, or an alkaline sulphuret, changes it to a dirty greenish black.

Hematosine differs from the other animal principles in containing as an essential ingredient a remarkable substance not found elsewhere in the animal system, viz., the oxide of the metal iron. If a little of the dried clot of blood be calcined in a crucible and digested with dilute hydrochloric acid, a solu-

tion will be obtained rich in oxide of iron; or if the solution of coloring matter just referred to, be treated with excess of chlorine gas, the yellow liquid separated from the grayish coagulum formed will be found to give in a striking manner the well-known reactions of peroxide of iron. There is little doubt either about the condition of the metal; oxide is withdrawn from the dry clot by the cautious addition of sulphuric acid, and without much alteration of the color of the mass.* It is well known that certain organic matters, as tartaric acid, prevent the precipitation of oxide of iron by alkalis, and its recognition by ferrocyanide of potassium, and it is very likely that the blood may contain a substance or substances capable of doing the same.

Hematosine, necessarily in a modified state, contains, according to Mulder, in 100 parts:

Carbon	66·49
Hydrogen	5·30
Nitrogen	10·50
Oxygen	11·05
Iron	6·66
	100†

The following table represents the composition of healthy human blood as a whole; it is on the authority of M. Lecanu.‡

	(1.)	(2.)
Water	780·15	785·58
Fibrine	2·10	3·57
Albumen	65·09	69·41
Coloring matter	133·00	119·63
Crystallizable fat	2·43	4·30
Fluid fat	1·31	2·27
Extractive matter, of uncertain nature, soluble in both water and alcohol	1·79	1·92
Albumen in combination with soda	1·26	2·01
Chlorides of sodium and potassium; carbonates, phosphates, and sulphates of potash and soda	8·37	7·30
Carbonates of lime and magnesia; phosphates of lime, magnesia, and iron; peroxide of iron	2·10	1·42
Loss	2·40	2·59
	1000·	1000·

* Liebig, Handwörtenbuch, i. p. 885.

† According to Mulder, hæmatosine may be represented by the formula $C_{44}H_{22}N_3O_6Fe$, the iron being in the metallic state, and the composition invariably the same, whether it be obtained from arterial or venous blood. The proof of the metallic condition of the iron depends on the fact that when dried coagulum or pure red particles of blood are digested in strong sulphuric acid, hydrogen gas is evolved, and after some days a solution of the sulphate of protoxide of iron is obtained and may be separated by the filter, while the insoluble red coloring matter will be left free from iron, but retaining its peculiar tint. Its formula is now $C_{44}H_{22}N_3O_6$. The difference of color between venous and arterial blood, in his opinion, is produced by a physical variation in the blood globules, producing a difference in the reflection of light, and the red coloring matter takes no part in the phenomena of respiration, the function of a carrier of oxygen being performed by the proteine of the blood, which, combining with oxygen in the capillaries of the lungs, changes the form and transparency of the envelop of the blood globules, and in the general capillary circulation is again decomposed with a consequent change of form and transparency. The blood globules of arterial blood being transparent convex bodies. and in venous blood semi-opaque concave mirrors.—Lond. Med. Gaz., Dec., 1844.—R. B.

‡ Ann. Chim. et de Phys., xlviii. p. 320.

In healthy individuals of different sexes these proportions are found to vary slightly, the fibrine and coloring matter being usually more abundant in the male than in the female; in disease, variations of a far wider extent are often apparent.

It appears singular that the red corpuscles, which are so easily dissolved by water, should remain uninjured in the fluid portion of the blood. This seems partly due to the presence of saline matter, and partly to that of albumen, the corpuscles being alike insoluble in a strong solution of salt and in a highly albuminous liquid. In the blood the limit of dilution within which the corpuscles retain their integrity appears to be nearly reached, for when water is added they immediately become attacked.

Closely connected with the subject of the composition of the blood are those of respiration, and of the production of animal heat.

The simplest view that can be taken of a respiratory organ in an air-breathing animal, is that of a little membranous bag, saturated with moisture, and containing air, over the surface of which meanders a minute blood-vessel, whose contents, during their passage, are thus subjected to the chemical action of that air through the substance of the membranes, and in virtue of the solubility of the gaseous matter itself in the water with which the membranes are imbued. In some of the lower classes of animals, where respiration is sluggish and inactive, these air-cells are few and large; but in the higher kinds they are minute, and greatly multiplied in number, in order to gain extent of surface, each communicating with the external air by the windpipe and its ramifications.

Respiration is performed by the agency of the muscles which lie between and about the ribs, and by the diaphragm. The lungs are not nearly emptied of air at each expiration. Under ordinary circumstances about 15 cubic inches only are thrown out, while by a forced effort as much as 50 or 60 cubic inches may be expelled. This is repeated about 18 times per minute, when the individual is tranquil and undisturbed.

The expired air is found to have undergone a remarkable change; it is loaded with aqueous vapor, while a very large proportion of oxygen has disappeared, and its place been supplied by carbonic acid; air *once* breathed containing enough of that gas to extinguish a taper. The total volume of the air seems to undergo but little change in this process, the carbonic acid being about equal to the oxygen lost. This, however, will probably be found to depend very much upon the nature of the food; it is likely that when fatty substances, containing much hydrogen, are used in large quantities, a disappearance of oxygen will be observed. Nitrogen is stated by some experimenters to be exhaled from the blood, which may sometimes happen. At any rate, no nitrogen is absorbed; the food invariably contains more of that element than the excretions.

Whatever may be the difficulties attending the investigation of these subjects,—and difficulties there are, as the discrepant results of the experiments prove,—one thing is clear; namely, that quantities of carbon, and possibly sometimes hydrogen, are daily oxidized in the body by the free oxygen of the atmosphere, and their products expelled from the system in the shape of carbonic acid and water. Now, if it be true that the heat developed in the act of combination is a constant quantity, and no proposition appears more reasonable, the high temperature of the body may be the simple result of this exertion of chemical force.

The oxidation of combustible matter in the blood is effected in the capillaries of the whole body, not in the lungs, the temperature of which does not exceed that of the other parts. The oxygen of the air is taken up in the lungs, and carried by the blood to the distant capillary vessels; by the aid of which, secre-

tion, and all the mysterious functions of animal life, are undoubtedly performed: here the *combustion* takes place, although how this happens, and what the exact nature of the combustible may be, beyond the simple fact of its containing carbon and hydrogen, yet remains a matter of conjecture. The carbonic acid produced is held in solution by the now venous blood, and probably confers, in great measure, upon the latter its dark color and deleterious action upon the nervous system. Once more poured into the heart, and by that organ driven into the second set of capillaries bathed with atmospheric air, this carbonic acid is conveyed outwards, through the wet membrane, by a kind of *false diffusion*, constantly observed under such circumstances; while at the same time oxygen is, by similar means, carried inwards, and the blood resumes its bright-red color, and its capability of supporting life. Much of this oxygen is, no doubt, simply dissolved in the serum: the corpuscles, according to Professor Liebig, act as carriers of another portion, in virtue of the iron they contain, that metal being alternately in the state of peroxide and of proto-carbonate; of peroxide in the arteries, and of carbonate of protoxide in the veins, by loss of oxygen, and acquisition of carbonic acid. M. Mulder considers the fibrine to act in this manner; being true fibrine in the veins, and, in part, at least, an oxide of proteine in the arteries. These views are ingenious, and quite consonant with all that is known on the subject: too much weight must not, however, be attached to any speculation of the kind.

It would be very desirable to show, if possible, that the quantity of combustible matter daily burned in the body is adequate to the production of the heating effects observed. Something has been done with respect to the carbon. Comparison of the quantities and composition of the food consumed by an individual in a given time, and of the excretions, shows an excess of carbon in the former over the latter, amounting, in some cases, according to Liebig's estimation,* to 14 ounces; the whole of which is thrown off in the state of carbonic acid, from the lungs and skin, in the space of twenty-four hours. This statement applies to the case of healthy, vigorous men, much employed in the open air, and supplied with abundance of nutritious food. Females, and persons of weaker habit, who follow in-doors pursuits in warm rooms, consume a much smaller quantity; their respiration is less energetic, and the heat generated less in amount. Those who inhabit very cold countries are well known to consume enormous quantities of food of a fatty nature, the carbon and hydrogen of which are, without doubt, chiefly employed in the production of animal heat. These people live by hunting: the muscular exertion required quickens and deepens the breathing; while, from the increased density of the air, a greater weight of oxygen is taken into the lungs, and absorbed into the blood at each inspiration. In this manner the temperature of the body is kept up, in spite of the piercing external cold; a most marvellous adjustment of the nature of the food, and even of the inclinations and appetite of the man to the circumstances of his existence, enable him to bear with impunity an atmospheric temperature which would otherwise destroy him.

The carbon consumed in respiration in one day by a horse moderately fed, amounted, in a valuable experiment of M. Boussingault, to 77 ounces; that consumed by a cow, to 70 ounces. The determination was made in the manner just mentioned, viz., by comparing the quantity and composition of the excretions with the quantity and composition of the food.

CHYLE.—A specimen examined by MM. Tiedemann and Gmelin, taken from the thoracic duct of a horse, was found closely to resemble, in composition and properties, ordinary blood; the chief difference was the comparative absence of coloring matter, the chyle having merely a reddish-white tint. It

* Animal Chemistry, p. 14.

coagulated, after standing four hours, and gave a red-colored clot, small in quantity, and a turbid, reddish-yellow serum. The milky appearance of chyle is due to fat globules, which sometimes confer the same character upon the serum of blood.

LYMPH.—Under the name of lymph, two or more fluids, very different in nature, have been confounded, namely, the fluid taken up by the absorbents of the alimentary canal, which is simply chyle, containing both fibrine and albumen, and the fluid poured out, sometimes in prodigious quantities, from serous membranes, which is a very dilute solution of albumen, containing a portion of soluble salts of the blood. The *liquor amnii* of the pregnant female, and the fluid of dropsy, are of this character.

MUCUS AND PUS.—The slimy matter effused upon the surface of various mucous membranes, as the lining of the alimentary canal, that of the bladder, of the nose, lungs, &c., to which the general name *mucus* is given, probably varies a good deal in its nature in different situations. It is commonly either colorless or slightly yellow, and translucent or transparent; it is quite insoluble in water, forming, in the moist state, a viscid, gelatinous mass. In dilute alkalis it dissolves with ease, and the solution is precipitated by an addition of acid.

Pus, the natural secretion of a wounded or otherwise injured surface, is commonly a creamy, white, or yellowish liquid, which, under the microscope, appears to consist of multitudes of minute globules. It is neither acid nor alkaline. Mixed with water, it communicates a milkiness to the latter, but after a time subsides. Caustic alkali does not dissolve pus, but converts it into a transparent, gelatinous substance, which draws out into threads. The peculiar *ropiness* thus produced with an alkali is the best character that can be given for distinguishing pus from mucus.

MILK, BILE, URINE, AND URINARY CALCULI.

MILK.—The peculiar special secretion destined for the nourishment of the young is, so far as is known, very much the same in flesh-eating animals and in those which live exclusively on vegetable food. The proportions of the constituents may, however, sometimes differ to a considerable extent. It will be seen hereafter that the substances present in milk are wonderfully adapted to its office of providing materials for the rapid growth and development of the animal frame. It contains an azotized matter, caseine, nearly identical in composition with muscular flesh, fatty principles, and a peculiar sugar, and, lastly, various salts, among which may be mentioned phosphate of lime, held in complete solution in a slightly alkaline liquid. This last is especially important to a process then in activity,—the formation of bone.

The white, and almost opaque, appearance of milk is an optical illusion; examined by a microscope of even moderate power, it is seen to consist of a perfectly transparent fluid, in which float about numbers of transparent globules; these consist of fat. It is a natural *emulsion*, or mechanical mixture of fatty matter with a watery solution.

When milk is suffered to remain at rest some hours at the ordinary temperature of the air, a large proportion of the fat globules collect at the surface into a layer of *cream*; if this be now removed and exposed for some time to strong agitation, the fat-globules coalesce into a mass, and the remaining watery liquid is expelled from between them and separated. The *butter* so produced must be thoroughly washed with cold water to remove as far as possible the last traces of caseine, which readily putrefies, and would in that case spoil the whole. A little salt is usually added.

Ordinary butter still, however, contains some butter-milk, and when intended

for keeping should be *clarified*, as it is termed, by fusion. The watery part then subsides, and carries with it the residue of the azotized matter. The flavor is unfortunately somewhat impaired by this process. The consistence of butter, in other words the proportions of margarine and oleine, is dependent upon the season, or more probably upon the kind of food; in summer, the oily portion is always more considerable than in winter. The volatile, odoriferous principle of butter, butyrine, has been already referred to.

The caseine of milk, in the state of cheese, is in many countries an important article of food. The milk is usually heated to about 120°, and coagulated by *rennet*, or an infusion of the stomach of the calf in water; the curd is carefully separated by a sieve from the whey, mixed with a due proportion of salt, and sometimes some coloring-matter, and then subjected to strong and increasing pressure. The fresh cheese so prepared being constantly kept cool and dry, undergoes a particular kind of putrefactive fermentation, very little understood, by which principles are generated which communicate a particular taste and odor. The goodness of cheese, as well as much of the difference of flavor perceptible in different samples, depends in great measure upon the manipulation; the best kinds contain a considerable quantity of fat, and are made with new milk; the inferior descriptions are made with skimmed milk.

Some of the Tartar tribes prepare a kind of spirit from milk by suffering it to ferment, with frequent agitation. The caseine converts a part of the milk-sugar into lactic acid, and another part into grape-sugar, which in turn becomes converted into alcohol. Mare's milk is said to answer better for this purpose than that of the cow.

In a fresh state, and taken from a healthy animal, milk is always feebly alkaline. When left to itself, it very soon becomes acid, and is then found to contain lactic acid, which cannot be discovered in the fresh condition. The alkalinity is due to the soda, which holds the caseine in solution. In this soluble form caseine possesses the power of taking up and retaining a very considerable quantity of phosphate of lime. The density of milk varies exceedingly; its quality usually bears an inverse ratio to its quantity. From a recent analysis of cow-milk in the fresh state by M. Haidlen,* the following statement of its composition in 1000 parts has been deduced:

Water	873·00
Butter	30·00
Caseine	48·20
Milk-sugar	43·90
Phosphate of lime	2·31
" magnesia	·42
" iron	·07
Chloride of potassium	1·44
" sodium	·24
Soda in combination with caseine	·42
	1000·

Human milk is remarkable for the difficulty with which it coagulates; it generally contains a larger proportion of sugar than cow-milk, but scarcely differs in other respects.

BILE.—This is a secretion of a very different character from the preceding; the largest internal organ of the body, the liver, is devoted to its preparation, which is said to take place from venous, instead of arterial blood. The com-

* Annalen der Chemie und Pharmacie, xlv. p. 263.

position of the bile has been made the subject of much investigation; the following is a summary of the most important facts which have been brought to light.

In its ordinary state bile is a very deep-yellow, or greenish, viscid, transparent liquid, which darkens by exposure to the air, and undergoes changes, which have been yet imperfectly studied. It has a disagreeable odor, a most nauseous bitter taste, a distinctly alkaline reaction, and is miscible with water in all proportions. When evaporated to dryness at 212°, and treated with alcohol, the greater part dissolves, leaving behind an insoluble jelly of mucus of the gall bladder. This alcoholic solution contains coloring matter and cholesterine; from the former it may be freed by digestion with animal charcoal, and from the latter by a large admixture of ether, in which the bile is insoluble, and separates as a thick, sirupy, and nearly colorless liquid. The coloring-matter may also be precipitated by barytic-water.

Pure bile thus obtained, when evaporated to dryness by a gentle heat, forms a slightly yellowish, brittle mass, resembling gum-Arabic. It is completely soluble in water and absolute alcohol. The solution is not affected by the vegetable acids; hydrochloric and sulphuric acids on the contrary give rise to turbidity, either immediately, or after a short interval. Acetate of lead partially precipitates it; the tribasic subacetate precipitates it completely; the precipitate is readily soluble in acetic acid, in alcohol, and to a certain extent in excess of acetate of lead. When carbonized by heat, and incinerated, bile leaves between 11 and 12 per cent. of ash, consisting chiefly of carbonate of soda, with a little common salt and alkaline phosphate. Bile seems in fact to be essentially a soda-salt of a peculiar acid, distantly resembling the resinous and fatty acids, susceptible of isolation, and to which the term *choleic* or *gallenic acid* is given.

Choleic acid is thus prepared: 8 parts of dry purified bile are dissolved in a quantity of alcohol, one part of oxalic acid deprived of its water of crystallization added, and the whole heated to ebullition. After twelve hours' rest the solution is filtered from the crystals of oxalate of soda, diluted with water, digested with carbonate of lead to remove excess of acid, filtered, and treated with sulphuretted hydrogen; the filtered liquid is lastly evaporated to dryness in a water-bath. The choleic acid much resembles pure bile, being an amorphous, yellowish brittle substance of excessively bitter taste, soluble in water and alcohol, but not in ether; it has, however, a strong acid reaction. A small addition of mineral acid occasions the precipitation of some of the substance from a watery solution, thereby causing turbidity; an excess redissolves it. When artificially combined with soda, it acquires all the properties of the original bile, with the exception of being rather more readily decomposed by an addition of acid.*

Choleic acid contains nitrogen; the formula to which Liebig gives the prefererence, and which agrees very well with the analytical results, is $C_{76}H_{66}N_2O_{22}$.

Choleic acid undergoes decomposition by both acids and alkalis; when boiled for several hours with moderately strong hydrochloric acid, it yields a brownish, pitch like, bitter, fusible substance, nearly insoluble in water and ether, but soluble in alcohol, to which the term *choloidic acid* is applied. It forms soluble salts with the alkalis, decomposes their carbonates with effervescence, and is composed of $C_{72}H_{56}O_{12}$. The acid mother-liquor contains a curious crystallizable substance called *taurine*, together with sal-ammoniac, and, if bile has been used instead of choleic acid, common salt. It is evaporated to a small bulk, filtered from the saline matter, and mixed with alcohol;

* Liebig, in Geiger's Pharmacie, i. p. 1570.

the taurine separates in small needles, and may be purified by recrystallization. When pure, it forms colorless, 4-sided prisms, which have no odor and very little taste; it is neutral to test-paper, permanent in the air, and easily soluble in water; in spirit of wine it dissolves to a very small extent, but is quite insoluble in absolute alcohol. Taurine is composed of $C_4H_7NO_{10}$,* or the elements of binoxalate of ammonia *plus* 2 eq. of water. Ox-bile yields taurine; that of man gives none.

Cholic acid is produced by boiling bile in a silver vessel with a very concentrated solution of caustic potash until ammonia ceases to be disengaged; water is added from time to time to prevent evaporation to dryness. The dark-colored soft mass is removed from the alkaline liquid, dissolved in water, acetic acid added in excess, and the whole mixed with two or three times its volume of ether, and agitated. The ethereal solution, left to evaporate spontaneously, deposits the cholic acid in crystals. When pure, it forms transparent tetrahedrons, and sometimes fine needles, which are transparent and colorless; it is easily soluble in alcohol and ether; but with difficulty in water; it has a bitter taste, an acid reaction, and forms soluble salts with the alkalis. Cholic acid contains $C_{74}H_{60}O_{18}$.

The coloring-matter of the bile forms the chief part of the concretions sometimes met with in the gall-bladders of oxen, and which are much valued by painters in water-colors, as forming a magnificent yellow pigment. It dissolves in caustic alkali without change of color, and when mixed with excess of nitric acid becomes successively green, blue, violet, red, and eventually yellow. The composition of this substance is unknown.

The once celebrated *oriental bezoar-stones*, are apparently biliary calculi, said to be procured from a species of antelope; they have a brown tint, a concentric structure, and a waxy appearance, and consist essentially of a peculiar and definite crystallizable principle, called *lithofellinic acid*. To procure this substance, the calculi are reduced to powder and exhausted with boiling alcohol; the dark solution is decolorized by animal charcoal, and left to evaporate by gentle heat, whereupon the lithofellinic acid is deposited in small, colorless, transparent six-sided prisms. It is insoluble in water, and with difficulty soluble in ether, but dissolves with ease in alcohol; it melts at 402°, and at a higher temperature burns with a smoky flame, leaving but little charcoal. Lithofellinic acid dissolves without decomposition in concentrated acetic acid, and in oil of vitriol; it forms a soluble salt with potash, and dissolves also in ammonia, but crystallizes out unchanged on evaporation. By analysis, lithofellinic acid is found to consist of $C_{40}H_{36}O_7$.

URINE.—The urine is the great channel by which the azotized matter of those portions of the body which have been taken up by the absorbents is conveyed away and rejected from the system in the form of urea; it serves also to remove superfluous water, and sometimes foreign soluble matters which get introduced into the blood.

The two most remarkable and characteristic constituents of urine, urea and uric acid, have already been fully described; in addition to these it contains phosphates of lime and magnesia, alkaline salts, lactic acid and lactates according to some, and certain yet imperfectly known principles, including an odoriferous and a coloring substance.

Healthy human urine is a transparent, light amber-colored liquid, which, while warm, emits a peculiar, aromatic, and not disagreeable odor. This is lost on cooling, while the urine at the same time occasionally becomes turbid from a deposition of urate of ammonia, which re-dissolves with the least ele-

* M. Redtenbacher has detected a considerable amount of sulphur in taurine, equal to 26 per cent.; this would make the composition, $C_4H_7NO_6S_2$.—R. B.

vation of temperature. It is very decidedly acid to test-paper; this acidity has been ascribed to free uric acid, and to free lactic acid; lactic acid can, however, hardly co-exist with urate of ammonia, and the amorphous buff-colored deposit obtained from fresh urine by spontaneous evaporation in vacuo is not uric acid, but the ammonia-salt of that substance. Dr. Bence Jones* has shown besides, that urate of ammonia itself has invariably, when in solution, a distinctly acid reaction, and that its solubility is increased, as before observed, by the presence of common salt, which is always found in the urine. That a free acid is sometimes present in the urine is certain, in this case the reaction to test-paper is far stronger, and the liquid deposits on standing, little, red, hard crystals of uric acid; but this is no longer a normal secretion.

The density of the urine varies from 1·005 to 1·035; about 1·020 to 1·023 may be taken as the average specific gravity. A high degree of density in urine may arise from an unusually large proportion of urea; in such a case the addition of nitric acid will occasion an almost immediate production of crystals of nitrate of urea, whereas with urine of the usual degree of concentration half an hour or more will elapse before the nitrate begins to separate. The quantity passed depends much upon circumstances, as, upon the activity of the skin; it is usually more deficient in quantity and of higher density in summer than in winter. Perhaps about 32 ounces in the 24 hours may be assumed as a mean.

When kept at a moderate temperature, urine quickly begins to decompose; it exhales an offensive odor, becomes alkaline from the production of carbonate of ammonia, and turbid from the deposition of earthy phosphates. The carbonate of ammonia is due to the putrefactive decomposition of the urea, which gradually disappears; the *ferment*, or active agent of the change, being apparently the mucus of the bladder, a portion of which is always voided with the urine. It has been found also that the yellow adhesive deposit from stale urine is a most powerful ferment to the fresh secretion. In this putrefied state urine is used in several of the arts, as in dyeing; and forms, perhaps, the most valuable manure for land known to exist.

Putrid urine always contains a considerable quantity of sulphuret of ammonium; this is formed by the deoxidation of sulphates by the organic matter. The highly offensive odor and extreme pungency of the decomposing liquid may be prevented by previously mixing the urine, as Liebig suggests, with sulphuric or hydrochloric acid, in sufficient quantity to saturate all the ammonia that can be formed.

An alkaline condition of the urine is sometimes met with, associated with a tendency to phosphatic deposits. Alkalinity can always be induced by the administration of neutral potash or soda-salts of a vegetable acid, as tartaric or acetic acid; the acid of the salt is burned in the blood in the process of respiration, and a portion of the base appears in the urine in the state of carbonate. The urine is often alkaline in cases of retention, from a commencement of putrefaction in the bladder itself; but this is easily distinguished from true alkalinity, in which it is *secreted* in that condition.

The following is an analysis of human urine by Berzelius. 1000 parts contained

* Report of Proceedings of Med. Chir. Society; Lancet, Dec. 16, 1843.

Water	933·00
Urea	30·10
Lactates and extractive matter*	17·14
Uric acid	1·00
Sulphates of potash and soda	6·87
Phosphate of soda	2·94
" of ammonia	1·65
" of lime and magnesia	1·00
Chloride of sodium	4·45
Sal-ammoniac	1·50
Silica	·03
Mucus of bladder	·32
	1000·

In certain states of disorder and disease substances appear in the urine which are never present in the normal secretion; of these the most common is albumen. This is easily detected by the addition of nitric acid in excess, which then causes a white cloud or turbidity, or by corrosive sublimate, the urine being previously acidified by a little acetic acid; boiling causes muddiness, or even in extreme cases a coagulum, which is insoluble in nitric acid. Mere turbidity by boiling is no proof of albumen, the earthy phosphates being often thrown down from nearly neutral urine under such circumstances; the phosphatic precipitate is, however, instantly dissolved by a drop of nitric acid.

In *diabetes* the urine contains grape-sugar, the quantity of which commonly increases with the progress of the disease, until it becomes enormous, the urine acquiring a density of 1·030 and beyond. It does not appear that the urea is deficient *absolutely*, although more difficult to discover from being mixed with such a mass of sirup. The smallest trace of sugar may be discovered in urine by Trommer's test formerly mentioned: a few drops of solution of sulphate of copper are added to the urine, and afterwards an excess of caustic potash; if sugar be present, a deep-blue liquid results, which, on boiling, deposits red suboxide of copper. With proper management, this test is very valuable; it will even detect sugar in the blood of diabetic patients.† Urine containing sugar, mixed with a little yeast, and put in a warm place, readily undergoes vinous fermentation, and afterwards yields, on distillation, weak alcohol, contaminated with ammonia.

The urine of children is said sometimes to contain benzoic acid; it is possible that this may be hippuric acid. When benzoic acid is taken, the urine after a few hours yields on concentration, and the addition of hydrochloric acid, needles of hippuric acid, soiled by adhering uric acid.

* All dark-colored, uncrystallizable substances, soluble both in water and alcohol, were confounded by the old chemists under the general name of *extractive matter*. The progress of modern science constantly tends to extricate from this confused mass one by one the many definite organic principles therein contained in more or less modified forms, and to restrict within narrower limits the application of the term. In the above instance, the coloring matter of the urine, and it may be several other substances, are involved.

Professor Liebig has quite recently published a very important paper on the urine; he states that all his endeavors to obtain direct evidence of the existence of lactic acid in that secretion, either in a fresh or putrid state, completely failed. Putrid urine yielded a volatile acid in notable quantity, which turned out to be acetic acid; a little benzoic acid was also noticed, and traced to a small amount of hippuric acid in the recent urine. The acid reaction of urine is ascribed to an acid phosphate of soda, produced by the partial decomposition of some of the common phosphate, the reaction of which is alkaline, by the organic acids (uric and hippuric) generated in the system, aided by the sulphuric acid constantly produced by the oxidation of the proteine-compounds of the food, or rather of the body.—*Lancet*, *June*, 1844.

† Dr. Jones, Med. Chirur. Trans., vol. xxvi.

The deposit of buff-colored or pinkish amorphous urate of ammonia which so frequently occurs in urine upon cooling after unusual exercise, or slight derangement of health, may be at once distinguished from a deposit of ammonio-magnesian phosphate by its instant disappearance on the application of heat. The earthy phosphates, besides, are never deposited from urine which has an acid reaction. The nature of the red coloring-matter which so often stains urinary deposits, especially in the case of free uric acid, is yet unknown.

The yellow principle of bile has been observed in urine in severe cases of jaundice.

The urine of the carnivorous mammifers is small in quantity, and highly acid; it has a very offensive odor, and quickly putrefies. In composition it resembles that of man, and is rich in urea. In birds and serpents the urine is a white, pasty substance, consisting almost entirely of urate of ammonia. In herbivorous animals it is alkaline and often turbid from earthy carbonates and phosphates; urea is still the characteristic ingredient, while of uric acid there is scarcely a trace; hippuric acid is usually, if not always, present, sometimes to a very large extent. When the urine putrefies, this hippuric acid, as already noticed, becomes changed to ammonia and benzoic acid.

Urinary calculi.—Stony concretions, differing much in physical characters and in chemical composition, are unhappily but too frequently formed in the bladder itself, and give rise to one of the most distressing complaints to which humanity is subject. Although many endeavors have been made to find some solvent or solvents for these calculi, and thus supersede the necessity of a formidable surgical operation for their removal, success has been but very partial and limited.

Urinary calculi are generally composed of concentric layers of crystalline or amorphous matter, of various degrees of hardness. Very frequently the central point or nucleus is a small foreign body: curious illustrations of this will be seen in any large collection. Calculi are not confined to man, the lower animals are subject to the same affliction; they have been found in horses, oxen, sheep, pigs, and almost constantly in rats.

The following is a sketch of the principal characters of the different varieties of calculi:—

1. *Uric acid.*—These are among the most common; externally they are smooth or warty, of yellowish or brownish tint; they have an imperfectly crystalline, distinctly concentric structure, and are tolerably hard. Before the blow-pipe the uric acid calculus burns away, leaving a minute quantity of ash, which is often alkaline. It is insoluble in water, but dissolves with facility in caustic potash, with but little ammoniacal odor; the solution mixed with acid gives a copious white, curdy precipitate of uric acid, which speedily becomes dense and crystalline. Cautiously heated with nitric acid, and then mixed with a little ammonia, it gives the characteristic reaction of uric acid, viz. deep purple-red murexide.

2. *Urate of ammonia.*—Calculi of urate of ammonia much resemble the preceding; they are easily distinguished, however. The powder boiled in water dissolves, and the solution gives a precipitate of uric acid when mixed with hydrochloric acid. It dissolves also in hot caustic potash with copious evolution of ammonia.

3. *Fusible calculus; phosphate of lime, with phosphate of magnesia and ammonia.*—This is one of the most common kinds. The stones are usually white or pale-colored, smooth, earthy, and soft; they often attain a large size. Before the blow-pipe this substance blackens from animal matter which earthy calculi always contain; then becomes white, and melts to a bead with comparative facility. It is insoluble in caustic alkali, but readily soluble in dilute

acids, and the solution is precipitated by ammonia. Calculi of unmixed phosphate of lime are very rare, as are also those of phosphate of magnesia and ammonia; the latter salt is sometimes seen forming small, brilliant crystals in cavities in the fusible calculus.

4. *Oxalate of lime calculus; mulberry calculus.*—The latter name is derived from the rough, warty character, and dark blood-stained aspect of this variety; it is perhaps the worst form of calculus. It is exceedingly hard; the layers are thick and imperfectly crystalline. Before the blow-pipe the oxalate of lime burns to carbonate by a moderate red heat, and when the flame is strongly urged, to quicklime. It is soluble in moderately strong hydrochloric acid, by heat, and very easily in nitric acid. When finely-powdered and long boiled in a solution of carbonate of potash, oxalate of potash may be discovered in the filtered liquid, when carefully neutralized by nitric acid, by white precipitates with solutions of lime, lead, and silver. A sediment of oxalate of lime in very minute, transparent, octahedral crystals, only to be seen by the microscope, is of common occurrence in urine in which a tendency to urate of ammonia deposit exists.

5. *Cystic and zanthic oxides* have already been described; they are very rare, especially the latter. Calculi of cystic oxide are very crystalline, and often present a waxy appearance externally; sediments of cystic oxide are sometimes met with. As before-mentioned, this substance is a definite crystallizable organic principle, containing sulphur to a large amount; it is soluble both in acids and alkalis. When the solution in nitric acid is evaporated to dryness, it blackens; when dissolved in a large quantity of caustic potash, a drop of solution of acetate of lead added, and the whole boiled, a black precipitate, containing sulphuret of lead, makes its appearance. By these characters cystic oxide is easily recognized.

Xanthic oxide, also a definite organic principle, is distinguished by the peculiar deep yellow color produced when its solution in nitric acid is evaporated to dryness; it is soluble in alkalis, but not in hydrochloric acid.

Very many calculi are of a composite nature, the composition of the different layers being occasionally changed, or alternating; thus urate of ammonia and oxalate of lime are not unfrequently associated in the same stone.

NERVOUS SUBSTANCE; MEMBRANOUS TISSUE; BONES.

Nervous substance.—The brain and nerves consist of a kind of half-coagulated albuminous substance, containing several remarkable fatty principles, capable of being extracted by alcohol and ether, some of which are yet very imperfectly known, and about 80 per cent. of water. Besides cholesterine, and a little ordinary fat, separated in the manner mentioned, M. Fremy* describes two new bodies, *cerebric acid* and *oleo-phosphoric acid.* The first is solid, white, and crystalline, soluble without difficulty in boiling alcohol, and forming with hot water a soft, gelatinous mass. It melts when heated, and decomposes almost immediately afterwards, exhaling a peculiar odor, and leaving a quantity of charcoal which contains free phosphoric acid, and is in consequence very difficult to burn. It combines with the alkalis, but forms insoluble compounds. Cerebric acid contains in 100 parts,

* Ann. Chim. et Phys., 3d Series, ii. p. 463.

Carbon	66·7
Hydrogen	10·6
Nitrogen	2·3
Oxygen	19·5
Phosphorus	·9
	100·

The oleo-phosphoric acid has been even less perfectly studied than the preceding substance. It is of soft, oily consistence, soluble in hot alcohol and ether, and saponifiable. When boiled with water, it is resolved into a fluid neutral oil, called *cebroleine*, and phosphoric acid, which dissolves.

The oily matter of the brain is sufficient in quantity to form with the albuminous portion a kind of emulsion, which, when beaten up, remains long suspended in water.

MEMBRANOUS TISSUES; SKIN.—The composition of the many gelatine-giving tissues of the body is in great measure unknown; even that of gelatine itself is very doubtful, as several different substances may very possibly be confounded under this name. Dr. Scherer* has given, among many others, analyses of the middle coat of the arteries, which will serve as an example of a finely-organized, highly-elastic membrane, and of the coarse epidermis of the sole of the foot, with which it may be contrasted.

	Artery coat.	Epidermis.
Carbon	53·75	51·04
Hydrogen	7·08	6·80
Nitrogen	15·36	17·23
Oxygen	23·81	24·93
	100·	100·

A little sulphur was found in the epidermis. Hair, horn, nails, wool, and feathers, have a nearly similar composition; they all dissolve with disengagement of ammonia in caustic potash, and the solution, when mixed with acid, deposits a kind of proteine, common to the whole. It is useless assigning formulæ to substances yet so little understood.

The principle of tanning, of such great practical value, is easily explained. When the skin of an animal, carefully deprived of hair, fat, and other impurities, is immersed in a dilute solution of tannic acid, the animal matter gradually combines with that substance as it penetrates inwards, forming a perfectly insoluble compound, which resists putrefaction completely; this is leather. In practice, lime-water is used for cleansing and preparing the skin, and an infusion of oak-bark, or sometimes catechu, or other astringent matter, for the source of tannic acid. The process itself is necessarily a slow one, as dilute solutions only can be safely used. Of late years, however, various contrivances, some of which show great ingenuity, have been adopted with more or less success, for quickening the operation. All leather is not tanned; glove-leather is dressed with alum and common-salt, and afterwards treated with a preparation of the yolks of eggs, which contain an albuminous matter and a yellow oil. Leather of this kind still yields size by the action of boiling water.

BONES.—Bones are constructed of a dense cellular tissue of membranous matter, made stiff and rigid by insoluble earthy salts, of which a peculiar phosphate of lime is the most abundant. The proportions of earthy and ani-

* Annalen der Chemie und Pharmacie, xl. p. 1.

mal matter vary very much with the kind of bone, and with the age of the individual, as will be seen in the following table, in which the corresponding bones of an adult and of a still-born child are compared.

	ADULT.		CHILD.	
	Inorganic matter.	Organic matter.	Inorganic matter.	Organic matter.
Femur	62·49	37·51	57·51	42·49
Humerus	63·02	36·98	58·08	41·92
Radius	60·51	39·49	56·50	43.50
Os temporum	63·50	36.50	55·90	44·10
Costa	57·49	42·51	53·75	46·25

The bones of the adult being constantly richer in earthy salts than those of the infant.

The following complete comparative analysis of human and ox-bones is due to Berzelius.

	Human bones.	Ox-bones.
Animal matter soluble by boiling	32·17	33·30
Vascular substance	1·13	
Phosphate of lime, with a little fluoride of calcium	53·04	57·35
Carbonate of lime	11·30	3·85
Phosphate of magnesia	1·16	2·05
Soda, and a little common-salt	1·20	3·45
	100·	100·

The teeth have a very similar composition, but contain less animal matter; their texture is much more solid and compact. The enamel does not contain more than 2 or 3 per cent. of animal matter.

ON THE FUNCTION OF NUTRITION IN THE ANIMAL AND VEGETABLE KINGDOMS.

The constant and unceasing waste of the animal body in the process of respiration, and in the various secondary changes therewith connected, necessitates an equally constant repair and renewal of the whole frame by the deposition or organization of matter from the blood, which is thus gradually impoverished. To supply this deficiency of solid material in the circulating fluid is the office of the food. The striking contrast which at first appears in the nature of the food of the two great classes of animals, the vegetable feeders and the carnivorous races, diminishes greatly on close examination; it will be seen that so far as the materials of blood, or, in other words, those devoted to the repair and sustenance of the body itself, are concerned, the process is the same. In a flesh-eating animal great simplicity is observed in the construction of the digestive organs; the stomach is a mere enlargement of the short and simple alimentary canal; and the reason is plain; the food of the creature, flesh, is absolutely identical in composition with its own blood, and with the body that blood is destined to nourish. In the stomach it undergoes mere solution, being brought into a state fitted for absorption by the lacteal vessels, by which it is nearly all taken up, and at once conveyed into the blood; the excrements of such animals are little more than the comminuted bones, feathers, hair, and other matters, which refuse to dissolve in the

stomach. The same condition, that the food employed for the nourishment of the body must have the same or nearly the same chemical composition as the body itself, is really fulfilled in the case of animals that live exclusively on vegetable substances. It has been shown* that certain of the azotized principles of plants, which often abound, and are never altogether absent, have a chemical composition and assemblage of properties which assimilate them in the closest manner, and it is believed even identify them, with the proteine-giving principles of the animal body; vegetable albumen, fibrine, and caseine are not to be distinguished from the bodies of the same name extracted from blood and milk.

If a portion of wheaten flour be made into a paste with water, and cautiously washed on a fine metallic sieve, or in a cloth, a grayish, adhesive, elastic, insoluble substance will be left, called *gluten*, and a milky liquid will pass through, which by few hours' rest becomes clear by depositing a quantity of starch. If now this liquid be boiled, it becomes again turbid from the production of a flocculent precipitate, which, when collected, washed, dried, and purified from fat by boiling with ether, is found to have the same composition as animal albumen. The gluten itself is a mixture of true vegetable fibrine, and a small quantity of a peculiar azotized matter called *gliadine*, to which its adhesive properties are due. The gliadine may be extracted by boiling alcohol, together with a thick, fluid oil, which is separable by ether; it is gluey and adhesive, quite insoluble in water, and, when dry, hard and translucent like horn; it dissolves readily in dilute caustic alkali, and also in acetic acid. The fibrine of other grain is unaccompanied by gliadine; barley and oatmeal yield no gluten, but incoherent filaments of nearly pure fibrine.

Vegetable albumen in a soluble state abounds in the juice of many soft succulent plants used for food: it may be extracted from potatoes by macerating the sliced tubers in cold water containing a little sulphuric acid. It coagulates when heated at a temperature dependent upon the degree of concentration, and cannot be distinguished when in this state from boiled white of egg in a divided condition.

Almonds, peas, beans, and many of the oily seeds contain a principle which bears the most striking resemblance to the caseine of milk. When a solution of this substance is heated, no coagulation occurs, but a skin forms on the surface, just as with boiled milk. It is coagulable by alcohol, and by acetic acid; the last being a character of importance. Such a solution mixed with a little sugar, an emulsion of sweet almonds for instance, left to itself, soon becomes sour and curdy, and exhales an offensive smell; it is then found to contain lactic acid.

All these substances dissolve in caustic potash with production of a small quantity of alkaline sulphuret; the filtered solutions mixed with excess of acid give precipitates of one and the same substance, proteine.

The following is the composition in 100 parts of vegetable albumen and fibrine; it will be seen that they agree very closely with the results before given.

	Albumen.	Fibrine.
Carbon	55·01	54·60
Hydrogen	7·23	7·30
Nitrogen	15·92	15·81
Oxygen, sulphur and phosphorus	21·84	22·29
	100.	100·

* Liebig, Ann. der Chem. und Pharm., xxxix. p. 129.

The composition of vegetable caseine, or *legumine*, has not been so well made out; so much discrepancy appears in the analyses as to lead to the supposition that different substances have been operated upon.

The great bulk, however, of the solid portion of the food of the herbivora consists of bodies which do not contain nitrogen, and therefore cannot yield sustenance in the manner described; some of these, as vegetable fibre or lignine, and waxy matter, pass unaltered through the alimentary canal; others, as starch, sugar, gum, and perhaps vegetable fat, are absorbed into the system, and afterwards disappear entirely: they are supposed to contribute very largely to the production of animal heat.

On these principles, Professor Liebig* has very ingeniously made the distinction between what he terms *plastic elements of nutrition*, and *elements of respiration;* to the former class belong

Vegetable fibrine,
Vegetable albumen,
Vegetable caseine,
Animal flesh,
Blood.

To the latter,

Fat,	Grape sugar,
Starch,	Milk sugar,
Gum,	Pectine,
Cane sugar,	Alcohol?

In a flesh-eating animal the waste of the tissues is very rapid, the temperature being, as it were, kept up in great measure by the burning of azotized matter; in a vegetable feeder it is probably not so great, the non-azotized substances being consumed in the blood in place of the organic fabric.

When the muscular movements of a healthy animal are restrained, a genial temperature kept up, and an ample supply of food containing much amylaceous or oily matter given, an accumulation of fat in the system rapidly takes place; this is well seen in the case of stall-fed cattle. On the other hand, when food is deficient, and much exercise is taken, emaciation results. These effects are ascribed to differences in the activity of the respiratory function; in the first instance, the heat-food is supplied faster than it is consumed, and hence accumulates in the form of fat; in the second, the conditions are reversed, and the creature is kept in a state of leanness by its rapid consumption. The fat of an animal appears to be a provision of nature for the maintenance of life during a certain period under circumstances of privation.

The origin of fat in the animal body has recently been made the subject of much animated discussion; on the one hand it is contended that satisfactory evidence exists of the conversion of starch and saccharine substances into fat, by a separation of carbon and oxygen, the change somewhat resembling that of vinous fermentation; it is argued on the other side, that oily or fatty matter is invariably present in the food supplied to the domestic animals, and that this fat is merely absorbed and deposited in the body in a slightly modified state. The question can only be decided by direct and most careful *quantitative* experiments, which are yet wanting.

It is not known in what manner *digestion*, the reduction in the stomach of the food to a nearly fluid condition, is performed. The natural secretion of that organ, the *gastric juice*, is said to contain a very notable quantity of free

* Animal Chemistry, p. 96.

hydrochloric acid. Dilute hydrochloric acid, aided by a temperature of 98° or 100°, dissolves coagulated albumen, fibrine, &c.; but many hours are required for the purpose. The gastric secretion has been supposed to contain a peculiar organic principle, called *pepsine*, said to have been isolated, to which this solvent power is, in conjunction with the hydrochloric acid, attributed. But an artificial mixture containing pepsine scarcely dissolves fibrine or boiled white of egg more easily than the dilute acid. The characters of pepsine itself also are so indefinite as to lead to great doubt of its individuality.*

The food of animals, or rather that portion of the food which is destined to the repair and renewal of the frame itself, is thus seen to consist of substances identical in composition with the body it is to nourish, or requiring but little chemical change to become so.

The chemical phenomena observed in the animal system resemble so far those produced out of the body by artificial means, that they are all, or nearly all, so far as is known, changes in a descending series; albumen and fibrine are probably more complex compounds than gelatine or the membrane which furnishes it; this in turn has a far greater complexity of constitution than urea, the regular form in which rejected azotized matter is conveyed out of the body. The animal lives by the assimilation into its own substance of the most complex and elaborate products of the organic kingdom; products which are, and, apparently, can only be, formed under the influence of vegetable life.

The existence of the plant is maintained in a manner strikingly dissimilar:—the food supplied to vegetables is *wholly inorganic;* the carbonic acid of the atmosphere, the water which falls as rain, or is deposited as dew; the minute trace of ammoniacal vapor present in the air; the alkali and saline matter extracted from the soil;—such are the substances which yield to plants the elements of their growth. That green healthy vegetables do possess, under circumstances to be mentioned immediately, the property of decomposing carbonic acid absorbed by their leaves from the air, or conveyed thither in solution through the medium of their roots, is a fact positively proved by direct experiment, and rendered certain by considerations of a very stringent kind. To effect this very remarkable decomposition, the influence of light is indispensable; the diffuse light of day suffices in some degree, but the direct rays of the sun greatly exalt the activity of the process. The carbon separated in this manner is retained in the plant in union with the elements of water, wit which nitrogen is also sometimes associated, while the oxygen is thrown off into the air from the leaves in a pure and gaseous condition.

The effect of ammoniacal salts upon the growth of plants is so remarkable as to leave little room for doubt concerning the peculiar function of the ammonia recently discovered in the air. Plants which in their cultivated state contain, and consequently require, a large supply of nitrogen, as wheat, and the cereals in general, are found to be greatly benefitted by the application to the land of such substances as putrefied urine, which may be looked upon as a solution of carbonate of ammonia, the *guano*† of the South Seas, which usually

* Among the substances necessary to the functions of digestion, diastase of animal origin has latterly been made to take a part. The view taken by Mialhe of digestion is, that the essential agents in this process are dilute acid, pepsine, and diastase, the two former being constituents of the gastric juice, the latter derived from the salivary and pancreatic glands. The action of the acid is to swell up and moisten the aliment, rendering it fit to be acted on by the pepsine. Under these circumstances fibrine, gluten and albumen dissolved in the weak acid exhibit many of the chemical properties of caseine, it is coagulated by pepsine, but the coagulum is immediately dissolved by an excess of this principle and completely changed in character. The pepsine has no influence on amylaceous matters, these are acted upon by the diastase and by conversion in dextrine and sugar become soluble.—R. B.

† Guano is the partially decomposed dung of birds; found in immense quantity on some of the barren islets of the western coast of South America, as that of Peru. More

contains a large proportion of ammoniacal salt, and even of pure sulphate of ammonia. Some of these manures doubtless owe a part of their value to the phosphates and alkaline salts they contain; still, the chief effect is certainly due to the ammonia.

Upon the members of the vegetable kingdom thus devolves the duty of building up, as it were, out of the inorganic constitutents of the atmosphere,—the carbonic acid, the water, and the ammonia,—the numerous complicated organic principles of the perfect plant, many of which are afterwards destined to become the food of animals, and of man. The chemistry of vegetable life is of a very high and mysterious order, and the glimpses occasionally obtained of its general nature are few and rare. One thing, however, is manifest, namely, the wonderful relations between the two orders of organized beings, in virtue of which the rejected and refuse matter of the one is made to constitute the essential and indispensable food of the other. While the animal lives, it exhales incessantly from its lungs, and often from its skin, carbonic acid; when it dies, the soft parts of its body undergo a series of chemical changes of *degradation*, which terminate in the production of carbonic acid, water, carbonate of ammonia, and, perhaps, other products in small quantity. These are taken up by a fresh generation of plants, which may in their turn serve for food to another race of animals.

recently, similar deposits have been found on the coast of Southern Africa. The guano now imported into England from these localities is usually a soft, brown powder of various shades of color. White specks of bone-earth, and sometimes masses of saline matter, may be found in it. That which is most recent, and probably most valuable as manure, often contains undecomposed uric acid, besides much oxalate or hydrochlorate of ammonia, and alkaline phosphates, and other salts; it has a most offensive odor. The specimens taken from older deposits have but little smell, are darker in color, contain no uric acid, and much less ammoniacal salt; the chief components are bone-earth, a peculiar dark-colored organic matter, and soluble inorganic salts.

SECTION IX.

ON CERTAIN PRODUCTS OF THE DESTRUCTIVE DISTILLATION AND SLOW PUTREFACTIVE CHANGE OF ORGANIC MATTER.

SUBSTANCES OBTAINED FROM TAR.

There are three principal varieties of tar: (1.) *tar of the wood-vinegar maker*, procured by the destructive distillation of dry, hard wood; (2. *Stockholm tar*, so largely consumed in the arts, as in ship-building, &c., which is obtained by exposing to a kind of rude *distillatio per descensum* the roots and useless parts of resinous pine and fir-timber; and lastly, (3.) *coal* or *mineral tar*, a by-product in the manufacture of coal-gas. This is viscid, black and ammoniacal.

All these tars yield by distillation, alone or with water, oily liquids of extremely complicated nature, from which a number of curious products, to be presently described, have been procured; the solid brown or black residue constitutes pitch. Hard-wood tar furnishes the following:

Paraffine; tar-oil stearine.—This remarkable substance is found in that part of the wood-oil which is heavier than water; it is extracted by redistilling the oil in a retort, collecting apart the last portions, gradually adding a quantity of alcohol, and exposing the whole to a low temperature. Thus obtained, paraffine appears in the shape of small, colorless needles, fusible at 110° to a clear liquid, which on solidifying becomes glassy and transparent. It is tasteless and inodorous; volatile without decomposition; and burns, when strongly heated, with a luminous yet smoky flame. It is quite insoluble in water; slightly soluble in alcohol; freely in ether; and miscible in all proportions, when melted, with both fixed and volatile oils. The most energetic chemical reagents, as strong acids, alkalis, chlorine, &c., fail to exert the smallest action on this substance; it is not known to combine in a definite manner with any other body, whence its extraordinary name, from *parum affinis*.

Paraffine contains carbon and hydrogen only, and in the same proportions as in olefiant gas, or C H. M. Leroy, of Copenhagen, makes it $C_{20}H_{21}$. The rational formula is of course unknown.

Eupione.*—This is the chief component of the light oil of wood-tar; it occurs also in the tar of animal matters, and in the fluid product of the distillation of rape-seed oil. Its separation is effected by the agency of concentrated sulphuric acid, or of a mixture of sulphuric acid and nitre, which oxidizes and destroys most of the accompanying substances. In a pure state it is an exceedingly thin, limpid, colorless liquid, of agreeable aromatic odor, but destitute of taste; it is the lightest known liquid, having a density of ·655. At 116° it boils and distils unchanged. Dropped upon paper, it makes a greasy stain, which after a time disappears. Eupione is very inflammable, and burns with a bright, luminous flame. In water it is quite insoluble, in rectified spirit nearly so, but with ether and oils freely miscible.

Eupione is a hydrocarbon; according to M. Hess, it consists of C_5H_6.

* From ευ, good, beautiful, and πιων, fat.

Other volatile oils, having a similar origin, and perhaps a similar composition, but differing from the above in specific gravity and boiling-point, are sometimes confounded with eupione. The study of these substances presents many serious difficulties. It is even doubtful whether the eupione be not *formed* by the energetic chemical agents employed in its supposed purification, and this remark applies with even greater force to the next three or four tar-products to be noticed.

PICAMAR.*—A component of the heavy oil of wood; it is a viscid, colorless, oily liquid, of feeble odor, but intensely bitter taste. Its density is 1·095, and it boils at 518°. It is insoluble in water, but dissolves in all proportions in alcohol, ether, and the oils. The most characteristic property of picamar is that of forming with the alkalis and ammonia crystalline compounds, which, although decomposed by water, are soluble without change in spirit. The composition of this substance is unknown.

KAPNOMOR.†—Such is the name given by Dr. Reichenbach to another oily liquid obtained from the same source as the last, by a long and complex process, in which strong solutions of caustic potash are freely used. It is described as a colorless, volatile oil, of high boiling-point, and rather lighter than water; it has an odor of ginger, and a taste, feeble at first, but afterwards becoming connected with an insupportable sense of suffocation. Water refuses to dissolve it; alcohol and ether take it up easily; and oil of vitriol combines with it, giving rise to a complex acid, the potash-salt of which is crystallizable. Its composition is unknown.

CEDRIRET.‡—The lighter oil of hard-wood tar contains a substance, separable from the eupione, &c., by caustic alkalis, which in contact with oxidizing agents, as persulphate of iron, chromic acid, or even atmospheric air, yields a mass of small, red, reticulated crystals, infusible by heat, and soluble in concentrated sulphuric acid with deep indigo-blue color. This substance is insoluble in water, alcohol, and ether; nothing is known respecting its composition.

PITTAKAL.—The name is derived from two Greek words signifying *pitch* or *resin*, and *beautiful;* it is found in the heavy oil of wood, but has been very imperfectly described. The characteristic property of pittakal is to form with barytes a compound which assumes in the air a fine purple or blue tint, gradually passing into black.

KREOSOTE.§—This is by far the most important and interesting body of the group; its discovery is due to Dr. Reichenbach; it is the principle to which wood-smoke owes its power of curing and preserving salted meat and other provisions. Kreosote is most abundantly contained in the heavy oil of beech-tar, as procured from the wood-vinegar maker, and is thence extracted by a most tedious and complicated series of operations; it certainly pre-exists, however, in the original material. The tar is distilled in a metallic vessel, and the different products collected apart; the most volatile portion, which is lighter than water, and consists chiefly of eupione, is rejected; the second portion is denser, and contains the kreosote, and is set aside; the distillation is stopped when paraffine begins to pass over in quantity. The impure kreosote is first agitated with carbonate of potash to remove adhering acid, separated, and re-distilled, the first part being again rejected; it is next strongly shaken with a solution of phosphoric acid, and again distilled; a quantity of ammonia is thus separated. Afterwards, it is dissolved in a solution of caustic

* From *pix*, and *amarus*, in allusion to its bitter taste.

† From *καπνος*, smoke. *μοιρα*, part.

‡ From *cedrium*, the old name for acid tar-water, and *rete*, a net.

§ Derived from Κρεας, flesh, and *σωζω*, I preserve.

potash of specific gravity 1·12, and decanted from the insoluble oil which floats on the surface; this alkaline liquid is boiled, and left some time in contact with air, by which it acquires a brown color from the oxidation of some yet unknown substance present in the crude product. The compound of kreosote and alkali is next decomposed by sulphuric acid; the separated kreosote again dissolved in caustic potash, boiled in the air, and the solution decomposed by acid, and this treatment repeated until the product ceases to become colored by the joint influence of oxygen and the alkaline base. When so far purified, it is well washed with water, and distilled from a little hydrate of potash. The first portion contains water; that which succeeds is pure kreosote.

In this condition kreosote is a colorless, somewhat viscid oily liquid of great refractive and dispersive power. It is quite neutral to test-paper; it has a penetrating and most peculiar odor, that, namely, of smoked meat, and a pungent and almost insupportable taste when placed in very small quantity upon the tongue. The density of this substance is 1·037, and its boiling-point 397° F. It inflames with difficulty, and then burns with a smoky light. When quite pure, it is inalterable by exposure to the air; much of the kreosote of commerce becomes, however, under these circumstances, gradually brown. 100 parts of cold water take up about 1¼ parts of kreosote; at a high temperature rather more is dissolved, and the hot solution abandons a portion on cooling. The kreosote itself absorbs water also to a considerable extent. In acetic acid it dissolves in much larger quantity. Alcohol and ether mix with kreosote in all proportions. Concentrated sulphuric acid, by the aid of heat, blackens and destroys it. Caustic potash dissolves kreosote with great facility, and forms with it a definite compound, which crystallizes in brilliant pearly scales.

Kreosote consists of carbon, hydrogen, and oxygen, but its exact composition is yet uncertain.

The most remarkable and characteristic feature of the compound in question is its extraordinary antiseptic power. A piece of animal flesh steeped in a very dilute solution of kreosote dries up to a mummy-like substance, but absolutely refuses to putrefy. The well-known efficacy of impure wood-vinegar in preserving provisions is with justice attributed to the kreosote it contains; and the effect of mere wood-smoke is also thus explained. In a pure state, kreosote is sometimes employed by the dentist for relieving toothache arising from putrefactive decay in the substance of the tooth.

Chrysen and Pyren.—M. Laurent extracted from pitch, by distillation at a high temperature, two new solid bodies, to which he gave the preceding names; they condense together, with a quantity of oily matter, partly in the neck of the retort, and partly in the receiver, and are separated by the aid of ether. *Chrysen*, so called from its golden color, is a pure yellow, crystalline powder, which fuses by heat, and sublimes without much decomposition. It is insoluble in water and alcohol, and nearly insoluble in ether; warm oil of vitriol dissolves it, with the development of a beautiful deep-green color. Boiling nitric acid converts it into an insoluble red substance, which has been studied. Chrysen is composed of C_3H. It has the same composition as *idrialine*, the fossil fat of the mercury mines of Idria.

Pyren differs from the preceding substance in being colorless, crystallizable in small, soft, micaceous scales, soluble in boiling alcohol and ether. It is fusible and volatile. Pyren contains C_5H_2.

Oil of ordinary tar, obtained by distillation alone, or with water, consists in great measure of unaltered oil of turpentine, mixed, however, with empyreumatic oily products, which give it a powerful odor and a dark color. The residual pitch contains much pine-resin, and thus differs from the solid portion of the hard-wood tar so frequently mentioned.

Volatile principles of coal-tar.

Coal-tar yields on distillation a large quantity of thin, dark-colored, volatile oil, which, when agitated with dilute sulphuric acid to remove ammonia, and twice rectified with water, becomes nearly colorless; it is very volatile, much lighter than water, very inflammable, and possesses in a high degree the property of dissolving caoutchouc, on which account it is very extensively used in the manufacture of water proof fabrics containing that material.

It appears that this coal-oil, or artificial naphtha, is a mixture of a number of hydrocarbons, some of which possess basic properties, and form crystallizable compounds with acids; at least a variety of different substances have been procured from the liquid in question; the remark formerly made respecting the doubtful pre-existence of substances thus obtained also applies here. The great bulk of the coal-oil appears to be made up of a neutral volatile oil, resembling eupione; the basic principles to be described constitute but a small part of the whole.*

KYANOL AND LEUKOL.—When a large mass of coal-oil is strongly agitated with concentrated solution of hydrochloric acid, an aqueous acid liquid results, which contains these substances, and is easily withdrawn from beneath the oily stratum by a siphon. By distillation with a slight excess of hydrate of lime, the acid is withdrawn, and the mixed bases, in a very impure condition, liberated. These, when separated and purified by methods too tedious to be here described, are thus distinguished:—*Kyanol* is a thin, oily, colorless liquid, of faint but agreeable vinous odor, and aromatic, burning taste; it is very volatile, but nevertheless has a high boiling-point, 358°. In the air it gradually becomes yellow, and acquires a resinous consistence. Its density is 1·028. Water dissolves kyanol to a certain extent, and also combines chemically with it, forming a hydrate; alcohol and ether are miscible with it in all proportions. Kyanol is quite destitute of alkaline reaction to test-paper, and in this respect differs from the volatile alkaloids of hemlock and tobacco, which in other respects it much resembles. The oxalate and the sulphate are the best-defined salts. The reaction with chloride of lime is exceedingly characteristic, and in fact gave name to the substance. A little of the oil dropped into a solution of this salt gives rise to a violet-colored, cloudy precipitate, which fills the entire vessel. The tint rapidly changes to dirty red; an effect which is accelerated by the addition of an acid.

Kyanol is composed of $C_{12}H_7N$.

Leukol has somewhat the odor of bitter-almonds; it is colorless, and considerably less volatile than the preceding substance. Its density is 1·081. It is slightly soluble in water, and miscible in all proportions with alcohol, ether, and essential oils. Leukol has no alkaline reaction, but forms salts with acids, which, generally speaking, are not so crystallizable as those of kyanol. It is unaffected by solution of bleaching-powder.

This substance contains $C_{18}H_8N$.

Another supposed component of coal-oil is *carbolic acid;* this is procured by the following process: 12 parts of the oil, 2 parts of hydrate of lime, and 50 parts of water, are intimately mixed, and left in contact for some time. The aqueous solution is then decomposed with hydrochloric acid, and the separated oil purified by cautious distillation, the first third only being collected. Pure carbolic acid is described as a colorless, oily liquid, which sometimes, under unknown circumstances, assumes a crystalline form. It has a very penetrating odor and burning taste, and destroys the skin. Its density is 1·062, and it boils at 386°. It is slightly soluble in water, destitute of acid reaction, and

* Hoffmann, Ann. der Chim. und Pharm., xlvii. p. 43.

forms with the alkalis a series of soluble crystallizable salts. Carbolic acid is described by M. Laurent under the name of *hydrate of phenyle*; it is composed of $C_{12}H_6O$.

Several other substances obtained from coal-oil have been incompletely described.

Naphthaline.—When, in the distillation of coal-tar, the last portion of the volatile oily product is collected apart and left to stand, a quantity of solid, crystalline matter separates, which is principally composed of the substance in question. An additional quantity may be obtained by pushing the distillation until the contents of the vessel begin to char; the naphthaline then condenses in the solid state, but dark-colored and very impure. By simple sublimation, once or twice repeated, it is obtained perfectly white. In this state naphthaline forms large, colorless, transparent, brilliant, crystalline plates, which exhale a faint and peculiar odor, which has been compared to that of the narcissus. Naphthaline melts at 176° to a clear, colorless liquid, which crystallizes on cooling; it boils at 413°, and evolves a vapor whose density is 4·528. When strongly heated in the air, it inflames and burns with a red and very smoky light. It is insoluble in cold water, but soluble to a slight degree at a boiling temperature; alcohol and ether dissolve it easily; a hot saturated alcoholic solution deposits fine iridescent crystals on cooling.

Naphthaline is found by analysis to contain $C_{10}H_4$.

Naphthaline dissolves in warm concentrated sulphuric acid, forming a red liquid, which, when diluted with water, and saturated with carbonate of baryta, yields salts of at least two distinct acids, analogous to sulphovinic acid. One of these, the *sulpho-naphthalic acid* of Mr. Faraday, crystallizes from a hot aqueous solution in small white scales, which are but sparingly soluble in the cold. The free acid is obtained in the usual manner by decomposing the baryta-salt with sulphuric acid; it forms a colorless, crystalline, brittle mass, of acid, metallic taste, very deliquescent, and very soluble in water. The second baryta-salt is still less soluble than the preceding. The composition of these substances is yet very uncertain.

Fuming nitric acid, at a high temperature, attacks naphthaline; the products are numerous, and have been attentively studied by M. Laurent. The same chemist has described a long series of curious products of the action of chlorine on naphthaline.

The history of the formation of naphthaline is rather interesting; it is, perhaps, the most stable of all the more complex compounds of carbon and hydrogen: in a vessel void of free oxygen it may be heated to any extent without decomposition; and indeed, where other carburets of hydrogen are exposed to a very high temperature, as by passing in vapor through a red-hot porcelain tube, a certain quantity of naphthaline is almost invariably produced. Hence its presence in coal and other tar is mainly dependent upon the temperature at which the destructive distillation of the organic substance has been conducted. Lamp-black very frequently contains naphthaline thus accidentally produced.

Paranaphthaline.—This substance occurs in the naphthaline of coal-tar, and is separated by the use of alcohol, in which ordinary naphthaline is freely soluble, but paranaphthaline almost totally insoluble; in other respects it much resembles naphthaline. The crystals obtained by sublimation are, however, usually smaller and less distinct. It melts at 356°, and boils at 570°, or above. Its best solvent is oil of turpentine. Paranaphthaline has the same composition as napththaline itself; the density of its vapor is, however, different, viz., 6·741. Its composition may be represented by the formula $C_{15}H_6$.

PETROLEUM, NAPHTHA, AND OTHER ALLIED SUBSTANCES.

Pit-coal, *lignite* or *brown coal*, *jet*, *bitumens* of various kind, *petroleum* or *rock-oil*, and *naphtha*, and a few other allied substances more rarely met with, are looked upon as products of the decomposition of organic matter, especially vegetable matter, beneath the surface of the earth; in situations where the conditions of contact with water, and nearly total exclusion of atmospheric air, are fulfilled. Deposited at the bottom of seas, lakes or rivers, and subsequently covered up by accumulations of clay and sand, hereafter destined to become shale and gritstone, the organic tissue undergoes a kind of fermentation by which the bodies in question, or certain of them, are slowly produced. Carbonic acid and carburetted hydrogen are by-products of the reaction; hence their frequent disengagement, the first from beds of lignite, and the second from the further advanced and more perfect coal.

The vegetable origin of coal has been placed beyond doubt by microscopic research; vegetable structure can be thus detected even in the most massive and perfect varieties of coal when cut into thin slices. In coal of inferior quality, much mixed with earthy matter, it is evident to the eye; the leaves of ferns, reeds, and other succulent plants, more or less resembling those of the tropics, are found in a compressed state between layers of shale or slaty clay, preserved in the most beautiful manner, but entirely converted into bituminous coal. The coal-mines of Europe, and particularly those of our own country, furnish an almost complete fossil flora; a history of many of the now lost species which once decorated the surface of the earth.

In the lignites the woody structure is much more obvious. Beds of this material are found in very many of the newer strata, above the true coal, to which they are consequently posterior. As an article of fuel, brown-coal is of comparatively small value; it resembles peat, giving but little flame and emitting a disagreeable, pungent smell.

Jet, used for making black ornaments, is a variety of lignite.

The true bitumens are destitute of all organic structure; they appear to have arisen from coal or lignite by the action of subterranean heat, and very closely resemble some of the products yielded by the destructive distillation of those bodies. They are very numerous, and have yet been but imperfectly studied.

1. *Mineral pitch*, or *compact bitumen*, the *asphaltum*, or *Jew's pitch* of some authors.—This substance occurs abundantly in many parts of the world; as, in the neighborhood of the Dead Sea in Judea; in Trinidad, in the famous *pitch lake*, and elsewhere. It generally resembles in aspect common pitch, being a little heavier than water, easily melted, very inflammable, and burning with a red, smoky flame. It consists principally of a substance called by M. Boussingault *asphaltene*, composed of $C_{20}H_{16}O_3$. It is worthy of remark, that M. Laurent found paranaphthaline in a native mineral pitch.

2. *Mineral tar* seems to be essentially a solution of asphaltene in an oily fluid called *petrolene*. This has a pale yellow color and peculiar odor; it is lighter than water, very combustible, and has a high boiling-point. It has the same composition as the oils of turpentine and lemon-peel, namely C_5H_4. Asphaltene contains, consequently, the elements of petrolene together with a quantity of oxygen, and probably arises from the oxidation of that substance.

3. *Elastic bitumen; mineral caoutchouc.*—This curious substance has only been found in three places: in a lead-mine at Castleton, in Derbyshire; at Montrelais, in France; and in the State of Massachusetts. In the two latter localities it occurs in the coal-series. It is fusible, and resembles in many respects the other bitumens.

Under the names *petroleum* and *naphtha* are arranged various mineral oils, which are observed in many places to issue from the earth, often in considerable abundance. There is every reason to suppose that these owe their origin to the action of internal heat upon beds of coal, as they are usually found in connection with such. The term *naphtha* is given to the thinner and purer varieties of rock-oil, which are sometimes nearly colorless; the darker and more viscid liquids bear the name of *petroleum*.

Some of the most noted localities of these substances are the following:—The North-west side of the Caspian Sea, near Baku, where beds of marl are found saturated with naphtha. Wells are sunk to the depth of about 30 feet, in which naphtha and water collect, and are easily separated. In some parts of this district so much combustible gas or vapor rises from the ground, that, when set on fire, it continues burning, and even affords heat for economical purposes. A large quantity of an impure variety of petroleum comes from the Birman territory in the East Indies; the country consists of sandy clay, resting on a series of alternate strata of sandstone and shale. Beneath these occurs a bed of pale blue shale loaded with petroleum, which lies immediately on coal. A petroleum-spring exists at Colebrook Dale, in Shropshire. The sea near the Cape de Verd Islands has been seen covered with a film of rock-oil. The finest specimens of naphtha are furnished by Italy, where it occurs in several places.

In proof of the origin attributed to these substances may be cited an experiment of Dr. Reichenbach, who, by distilling with water about 100 lbs. of pit-coal, obtained nearly two ounces of an oily liquid exactly resembling the natural naphtha of Amiano in the Duchy of Parma.

The variations of color and consistence in different specimens of these bodies certainly depends in great measure upon the presence of pitchy and fatty substances dissolved in the more fluid oil. Dr. Gregory found paraffine in petroleum from Rangoon.

The boiling-point of rock-oil varies from about 180° to near 600°: a thermometer inserted into a retort in which the oil is undergoing distillation, never shows for any length of time a constant temperature. Hence, it is inferred to be a mixture of several different substances. Neither do the different varieties of naphtha give similar results on analysis; they are all, however, carburets of hydrogen. The use of these substances in the places where they abound is tolerably extensive; they often serve the inhabitants for fuel, light, &c. To the chemist pure naphtha is valuable, as offering facilities for the preservation of the more oxidable metals, as potassium and sodium.

The following are of rarer occurrence.

Retinite, or *Retinasphalt*, is a kind of fossil resin met with in brown coal; it has a yellow or reddish color, is fusible and inflammable, and readily dissolved in great part by alcohol. The soluble portion, the *retinic acid* of Prof. Johnstone, contains $C_{21}H_{14}O_5$. *Hatchetine* is a somewhat similar substance met with in mineral coal at Merthyr-Tydvil, and also near Loch Fyne, in Scotland. *Idrialine* has been already mentioned; it is found associated with native cinnabar, and is extracted from the ore by oil of turpentine, in which it dissolves. It is a white, crystalline substance, scarcely volatile without decomposition, but slightly soluble in alcohol and ether, and composed of C_3H.

Ozokerite or *fossil wax*, is found in Moldavia, in a layer of bituminous shale; it is brownish, and has a somewhat pearly appearance; it is fusible below 212°, and soluble with difficulty in alcohol and ether, but easily in oil of turpentine. It appears to contain more than one definite principle.

APPENDIX.

ON THE EQUIVALENT NUMBERS.

The table of equivalent numbers given in the body of the work at p. 152 is chiefly taken from the tables of the *Lehrbuch* of Berzelius, being, in great measure, the results of the inquiries of that distinguished philosopher. The equivalents of arsenic, antimony, phosphorus, and columbium have been doubled from motives of convenience. The equivalents of a few of the more important substances have been revised by subsequent investigations, and the altered numbers have been adopted in certain cases mentioned below.

Calcium.—Dumas,* and Erdmann and Marchand,† make the equivalent of calcium exactly 20. This differs somewhat from the *most recent* determination of Berzelius‡ by a different process, viz., 20·15. The former number has been provisionally adopted.

Carbon.—The equivalent of carbon deduced by Dumas from his experiments on the combustion of the diamond§ is exactly 6. Similar experiments by Erdmann and Marchand‖ lead to the like conclusion. The numbers deduced by MM. Liebig and Redtenbacher¶ from the analysis of certain silver-salts of organic acids is 6·07; which, after all, does not differ *very* considerably from the whole number. Baron von Wrede,** again, makes the density of oxygen 1·1052, and that of carbonic acid 1·5204; the difference, ·4152 referred to the oxygen, gives the combining number for carbon=6·01. The whole number has been adopted.

Chlorine.—It is exceedingly important that the equivalent of chlorine should be well established. The method adopted by Berzelius,†† and which also has been followed by Dr. Turner,‡‡ Pelouze,§§ and Marignac,‖‖ consists in decomposing by heat a known weight of pure and dry chlorate of potash, and thus determining the relation between the equivalent of chloride of potassium and that of oxygen, the number 8 being assumed for the latter. The proportions in which silver and chlorine unite are then determined by direct experiment; and lastly, the quantity of chloride of silver produced from a

* Comptes rendus, xiv. p. 537.
† Ann. Chim. et Phys., 3d Series, viii. p. 207.
‡ Annalen der Chemie und Pharmacie, xlvi. p. 241.
§ Ann. Chim. et Phys., 3d Series, i. p. 5.
‖ Annalen der Chem. und Pharm., xliv. p. 210.
¶ Idem., xxxviii. p. 113.
** Idem., xliv. p. 211.
†† Lehrbuch, v. p. 106.
‡‡ Phil. Trans. for 1833, p. 523.
§§ Comptes rendus, xiv. p. 950.
‖‖ Annalen der Chem. und Pharm., xliv. p. 11.

known weight of chloride of potassium is ascertained. Thus, in the experiment of Berzelius first referred to, 100 parts chlorate of potash yielded 60·85 parts chloride of potassium, and 39·15 parts oxygen. From chlorate of potash 6 equivalents of oxygen are disengaged by heat; consequently,

$$\frac{39{\cdot}15}{6} = 6{\cdot}525;$$

or the numbers 6·525 and 60·85 represent the relative weights of equivalents of oxygen and of chloride of potassium. Making the former = 8, we have by simple proportion,

$$6{\cdot}525 \quad : \quad 8 \quad :: \quad 60{\cdot}85 \quad : \quad 74{\cdot}6005,$$

the real equivalent of chloride of potassium.

Again, 100 parts of pure silver, by solution in nitric acid and precipitation by a soluble chloride, yield 132·75 parts of dry chloride of silver; and further, 100 parts of pure chloride of potassium, dissolved in water and precipitated by nitrate of silver in excess, furnish 192·4 parts of chloride of silver. Hence,

Chlor. silver.		Chlorine.		Chlor. silver.		Chlorine.
132·75	:	32·75	: :	192·4	:	47·465

the quantity of chlorine contained in 100 parts of chloride of potassium. Consequently,

Chlor. potass.		Chlorine.		Eq. of chlor. potass.		Eq. of chlorine.
100	:	47·465	: :	74·6005	:	35·41

From the preceding data the equivalents of silver and potassium are also easily determined:—

132·75 parts of chloride of silver contain 32·75 parts chlorine and 100 parts silver; consequently,

$$32{\cdot}75 \quad : \quad 100 \quad :: \quad 35{\cdot}41 \quad : \quad 108{\cdot}12$$

the equivalent of silver. Also,

100 parts of chloride of potassium = 47·465 parts chlorine and 52·535 parts potassium; hence,

$$47{\cdot}465 \quad : \quad 52{\cdot}535 \quad :: \quad 35{\cdot}41 \quad : \quad 39{\cdot}19$$

Dr. Turner's equivalent of chlorine is 35·42; that of Marignac is 35·37; and lastly, the number found by Dr. Penny,* by a somewhat different method, is 35·45. The original equivalent of Berzelius is retained in the table.

Nitrogen.—The density of nitrogen is, according to Dumas, ·972; and that of oxygen, 1·1057. In binoxide of nitrogen equal measures of the gases are combined; or, by weight, 1 equivalent nitrogen to 2 equivalents oxygen. Hence, the combining number of nitrogen is ascertained by a simple rule of proportion:—

$$1{\cdot}1057 \quad : \quad {\cdot}972 \quad :: \quad 16 \quad : \quad 14{\cdot}06.$$

Zinc.—M. Favre* has quite recently re-determined the equivalent of zinc by two different methods of investigation; namely, by analysis of the oxalate, and by observing the quantity of hydrogen, estimated in the state of water

* Phil. Trans. for 1839, p. 13.

after combustion by ignited oxide of copper, disengaged during the solution in an acid of a known weight of pure zinc. The first experiments gave as a mean the number 33·01; and the second set, 32·97. The whole number, 33, has therefore been taken.

Uranium.—The equivalent of uranium is that of M. Péligot.

HYDROMETER TABLES.

COMPARISON OF THE DEGREES OF BAUMÉ'S HYDROMETER, WITH THE REAL SPECIFIC GRAVITIES.

1. *For Liquids heavier than Water.*

Degrees.	Specific gravity.	Degrees.	Specific gravity.	Degrees.	Specific gravity
0	1·000	26	1·206	52	1·520
1	1·007	27	1·216	53	1·535
2	1·013	28	1·225	54	1·551
3	1·020	29	1·235	55	1·567
4	1·027	30	1·245	56	1·583
5	1·034	31	1·256	57	1·600
6	1·041	32	1·267	58	1·617
7	1·048	33	1·277	59	1·634
8	1·056	34	1·288	60	1·652
9	1·063	35	1·299	61	1·670
10	1·070	36	1·310	62	1·689
11	1·078	37	1·321	63	1·708
12	1·085	38	1·333	64	1·727
13	1·094	39	1·345	65	1·747
14	1·101	40	1·357	66	1·767
15	1·109	41	1·369	67	1·788
16	1·118	42	1·381	68	1·809
17	1·126	43	1·395	69	1.831
18	1·134	44	1·407	70	1·854
19	1·143	45	1·420	71	1·877
20	1·152	46	1·434	72	1·900
21	1·160	47	1·448	73	1·924
22	1·169	48	1·462	74	1·949
23	1·178	49	1·476	75	1·974
24	1·188	50	1·490	76	2·000
25	1·197	51	1·495		

2. *Baumé's Hydrometer for Liquids lighter than Water.*

Degrees.	Specific gravity.	Degrees.	Specific gravity.	Degrees.	Specific gravity.
10	1·000	27	·896	44	·811
11	·993	28	·890	45	·807
12	·986	29	·885	46	·802
13	·980	30	·880	47	·798
14	·973	31	·874	48	·794
15	·967	32	·869	49	·789
16	·960	33	·864	50	·785
17	·954	34	·859	51	·781
18	·948	35	·854	52	·777
19	·942	36	·849	53	·773
20	·936	37	·844	54	·768
21	·930	38	·839	55	·764
22	·924	39	·834	56	·760
23	·918	40	·830	57	·757
24	·913	41	·825	58	·753
25	·907	42	·820	59	·749
26	·901	43	·816	60	·745

These two tables are on the authority of M. Francœur:—they are taken from the *Handwörterbuch der Chemie* of Liebig and Poggendorff. Baumé's hydrometer is very commonly used on the Continent, especially for liquids heavier than water. For lighter liquids the hydrometer of Cartier is often employed in France. Cartier's degrees differ but little from those of Baumé.

In the United Kingdom Twaddell's hydrometer is a good deal used for dense liquids. This instrument is so graduated that the real sp. gr. can be deduced by an extremely simple method from the degree of the hydrometer, namely, by multiplying the latter by 5, and adding 1000; the sum is the sp. gr., water being 1000. Thus 10° Twaddell indicates a sp. gr. of 1050, or 1·05; 90° Twaddell, 1450, or 1·45.

In the Customs and Excise Syke's hydrometer is used.

ABSTRACT

OF DR. DALTON'S TABLE OF THE ELASTIC FORCE OF VAPOR OF WATER AT DIFFERENT TEMPERATURES, EXPRESSED IN INCHES OF MERCURY.

Temp.	Force.	Temp.	Force.	Temp.	Force.
32°	·200	57°	·474	90°	1·36
33	·207	58	·490	95	1·58
34	·214	59	·507	100	1·86
35	·221	60	·524	105	2·18
36	·229	61	·542	110	2·53
37	·237	62	·560	115	2·92
38	·245	63	·578	120	3·33
39	·254	64	·579	125	3·75
40	·263	65	·616	130	4·34
41	·273	66	·635	135	5·00
42	·283	67	·665	140	5·74
43	·294	68	·676	145	6·53
44	·305	69	·698	150	7·42
45	·316	70	·721	160	9·46
46	·328	71	·745	170	12·13
47	·339	72	·770	180	15·15
48	·351	73	·796	190	19·00
49	·363	74	·823	200	23·64
50	·375	75	·851	210	28·84
51	·388	76	·880	212	30·00
52	·401	77	·910	220	34·99
53	·415	78	·940	230	41·75
54	·429	79	·971	240	49·67
55	·443	80	1·000	250	58·21
56	·458	85	1·170	300	111·81

ABSTRACT

OF THE TABLE OF LÖWITZ, SHOWING THE PROPORTION BY WEIGHT OF ABSOLUTE OR REAL ALCOHOL IN SPIRITS OF DIFFERENT DENSITIES.*

Sp. gr. at 60°	Per cent. of real alcohol.	Sp. gr. at 60°	Per cent. of real alcohol.	Sp. gr. at 60°	Per cent. of real alcohol.
0·796	100	0·881	66	0·955	32
0·798	99	0·883	65	0·957	31
0·801	98	0·886	64	0·958	30
0·804	97	0·889	63	0·960	29
0·807	96	0·891	62	0·962	28
0·809	95	0·893	61	0·963	27
0·812	94	0·896	60	0·965	26
0·815	93	0·898	59	0·967	25
0·817	92	0·900	58	0·968	24
0·820	91	0·902	57	0·970	23
0·822	90	0·904	56	0·972	22
0·825	89	0·906	55	0·973	21
0·827	88	0·908	54	0·974	20
0·830	87	0·910	53	0·975	19
0·832	86	0·912	52	0·977	18
0·835	85	0·915	51	0·978	17
0·838	84	0·917	50	0·979	16
0·840	83	0·920	49	0·981	15
0·843	82	0·922	48	0·982	14
0·846	81	0·924	47	0·984	13
0·848	80	0·926	46	0·986	12
0·851	79	0·928	45	0·987	11
0·853	78	0·930	44	0·988	10
0·855	77	0·933	43	0·989	9
0·857	76	0·935	42	0·990	8
0·860	75	0·937	41	0·991	7
0·863	74	0·939	40	0·992.	6
0·865	73	0·941	39		
0·867	72	0·943	38		
0·870	71	0·945	37		
0·872	70	0·947	36		
0·874	69	0·949	35		
0·875	68	0·951	34		
0·879	67	0·953	33		

* From Dr. Turner's Elements.

WEIGHTS AND MEASURES.

480·	grains, Troy	= 1 oz. Troy.
437·5	„	= 1 oz. Avoirdupoids.
7000·	„	= 1 lb. Avoirdupoids.
5760·	„	= 1 lb. Troy.

The imperial gallon contains of water, at 60°,	70,000·	grains,
The pint ($\frac{1}{8}$th of gallon)	8,750·	„
The fluidounce ($\frac{1}{20}$th of pint)	437·5	„

The pint equals 34·66 cubic inches.*

The French *kilogramme* = 15433·6 grains, or 2·679 lbs. Troy or 2·205 lbs. Avoirdupoids.

The *gramme*	=	15·4336	grains.
„ *decigramme*	=	1·5434	„
„ *centigramme*	=	·1543	„
„ *milligramme*	=	·0154	„

The *mètre* of France	=	39·37	inches.
„ *decimètre*	=	3·937	„
„ *centimètre*	=	·394	„
„ *millimètre*	=	·0394	„

* Apothecaries' or wine measure, U. S.

The wine gallon contains of water, at 60°,	58·329	grains.
The pint ($\frac{1}{8}$th of gallon(.	7·291	„
The fluid-ounce ($\frac{1}{16}$th of pint) . . .	456	„

The pint equals 28·875 cubic inches.—R. B.

DR. SCHWEITZER'S

OF THE PRINCIPAL MINERAL WATERS OF GERMANY AND

Grains of Anhydrous Ingredients in One pound Troy.	Carlsbad.	Ems.	Schlesischer Obersalzbrunnen.
Carbonate of Soda - -	7·2712	8·0625	7.6211
Ditto of Lithia - -	0·0150	0·0405	- -
Ditto of Baryta - -	- -	0·0022	- -
Ditto of Strontia - -	0·0055	0·0080	0·0170
Ditto of Lime - -	1·7775	0·8555	1·5464
Ditto of Magnesia - -	1·0275	0·5915	1·5496
Ditto (Proto) of Manganese	0·0048	0·0028	0·0026
Ditto (Proto) of Iron -	0·0208	0·0120	0·0356
Sub-Phos. of Lime - -	0·0012	- -	- -
Ditto of Alumina - -	0·0019	0·0014	- -
Sulphate of Potassa -	- -	0·4050	0·3160
Ditto of Soda - -	14·9019	- -	2·5106
Ditto of Lithia - -	- -	- -	- -
Ditto of Lime - -	- -	- -	- -
Ditto of Strontia - -	- -	- -	- -
Ditto of Magnesia - -	- -	- -	- -
Nitr. of Magnesia - -	- -	- -	- -
Chlor. of Ammonium -	- -	- -	0·0164
Ditto of Potassium -	- -	0·0338	- -
Ditto of Sodium - -	5·9820	5·7255	0·8682
Ditto of Lithium - -	- -	- -	- -
Ditto of Calcium - -	- -	- -	- -
Ditto of Magnesium -	- -	- -	- -
Ditto of Barium - -	- -	- -	- -
Ditto of Strontium - -	- -	- -	- -
Bromide of Sodium -	- -	- -	0·0051
Iodide of Sodium - -	- -	- -	- -
Fluoride of Calcium -	0·0184	0·0014	- -
Alumina - - -	- -	- -	- -
Silica - - - -	0·4329	0.3104	0·2423
Total - - -	31·4606	16·0525	14·7309
Carbonic Acid Gas in 100 cubic inches	58	51	98
Temperature (F.)	Sprud. 165° Neub. 138° Mühl. 128° Ther. 122°	Kess. 117° Krän. 84°	58°
Analyzed by - - -	Berzelius.	Struve.	Struve.

TABLE OF ANALYSES

OF THE SARATOGA CONGRESS SPRING OF AMERICA.

Saratoga Congress Spring.	Kissengen. Ragozi.	Marienbad. Kreutzbr.	Auschowitz. Ferdinands-brunnen.	Eger. Franzens. brunnen.
0·8261	- -	5·3499	4·5976	3·8914
- -	- -	0·0858	0·0507	0·0282
- -	- -	- -	- -	- -
0·0672	0·0592	0·0028	0·0040	0·0023
5·8531	4·8180	2·9509	3·0085	1·3501
4·1155	1·3185	2·0390	2·2867	0·5040
0·0202	0·0121	2·0288	0·0692	0·0322
0·0173	0·1397	0·1319	0·2995	0·1762
- -	- -	- -	- -	0·0172
- -	- -	- -	0·0040	0·0092
0·1379	1·2540	- -	- -	- -
- -	- -	28·5868	16·9022	18·3785
- -	- -	- -	- -	- -
- -	5·5485	- -	- -	- -
- -	- -	- -	- -	- -
- -	- -	- -	- -	- -
0·1004	- -	- -	- -	- -
0·0326	0·0364	- -	- -	- -
1·6256	- -	- -	- -	- -
19·6653	39·3733	10·1727	6.7472	6·9229
- -	- -	- -	- -	- -
- -	- -	- -	- -	- -
- -	3·6599	- -	- -	- -
- -	- -	- -	- -	- -
- -	- -	- -	- -	- -
0·1613	0·3331	- -	- -	- -
0·0046	- -	- -	- -	- -
- -	- -	- -	- -	- -
0·0069	- -	0·0023	- -	- -
0·1112	0·1609	0·2908	0·5023	0·3548
32·7452	56·7136	49·6417	34.4719	31·6670
114	96	105	146	154
50°	53°	53°	49°	54°
Schweitzer.	Struve.	Berzelius.	Steinmann.	Berzelius.

INDEX.

A.

Absorption of heat, 65
Acetal, 328
Acetone, 332
Acetyle-compounds, 326
Acid, acetic, 328
 aconitic, or equisetic, 359
 aldehydic, 327
 alloxanic, 383
 amygdalinic 368
 anilic, or indigotic, 395
 anthranilic, 396
 antimonious, 255
 antimonic, 255
 arsenious, 258
  tests for, 259
 arsenic, 259
 aspartic, 393
 benzilic, 350
 benzoic, 346
 boracic, 131
 bromic, 128
 butyric, 402
 capric and caproic, 402
 carbolic, 435
 carbonic, 110
  liquefaction of, 50
 cerebric, 425
 choleic, or galenic, 420
 chloracetic, 331
 chloro-carbonic, 112
 chloro-chromic, 250
 chloro-sulphuric, 321
 chloro-valerisic, 344
 chloric, 125
 chlorous, 124
 cholic, 421
 choloidic, 420
 chromic, 249
 chrysammic, 396
 chrysanilic, 396
 chrysolepic, 396
 cinnamic, 353
 citric, 359
 cocinic, 401
 columbic, 254
Acid, comenic, 390
 croconic, 306
 cyanic, 371
 cyanuric, 372
 dialuric, 385
 elaidic, 402
 ethalic, 403
 ethionic, 323
 ferric, 230
 formic, 340
 fulminic, 373
 fumaric, 360
 gallic, 362
 hippuric, 350
 hydriodic, 127
 hydrobromic, 128
 hydrochloric, 121
 hydrocyanic, 365
 hydroferrocyanic, 375
 hydrofluoric, 129
 hydrofluosilicic, 130
 hydrosalicylic, 352
 hydrosulphuric, 142
 hydrosulphocyanic, 379
 hyperchloric, 125
 hyperiodic, 127
 hypermanganic, 228
 hyperchlorous, 124
 hypophosphorous, 119
 hyponitrous, 107
 hyposulphurous, 116
 hyposulphuric, 116
 iodic, 127
 isethionic, 323
 japonic, 362
 kakodylic, 336
 kinic, 390
 lactic, 310
 lithofellinic, 421
 maleic, 360
 malic, 360
 mandelic, 349
 manganic, 227
 margaric, 399
 meconic, 389
 melanic, 352
 mellitic, 306

Acid, mesoxalic, 383
metagallic, 363
metaphosphoric, 187
metapectic, 302
molybdic, 253
mucic, 306
muriatic, 121
mykomelinic, 383
myristic, 402
myronic, 405
nitric, 105
nitrous, 108
œnanthic, 315
oleic, 400
oleo-phosphoric, 425
osmic, 279
oxalic, 303
oxalovinic, 317
oxaluric, 384
palmitic, 401
parabanic, 384
pectic, 302
phocenic, 402
phosphovinic, 316
phosphoric, 119, 185
phosphorous, 119
pyro-gallic, 363
pyro-phosphoric, 186
pyro-tartaric, 358
pyro-meconic, 390
picric, or carbazotic, 395
pinic, sylvic and pimaric, 405
racemic, 358
retinic, 438
rhodizonic, 306
rubinic, 362
saccharic, 305
salicylic, 352
sebacic, 402
selenic, 117
selenious, 117
silicic, 129
stearic, 399
suberic, 306, 402
succinic, 402
sulphuric, 114
sulphurous, 113
sulphuretted-hyposulphuric, 116
sulphovinic, 316
sulphomethylic, 339
sulphoglyceric, 401
sulphonaphthalic, 436
sulphosaccharic, 297
sulphobenzoic, 247
Acid, sulphindigotic, 394
tannic, 361
tartaric, 356
thionuric, 384
titanic, 254
ulmic, 298
uramilic, 385
uric, 424
valerianic, 344
vanadic, 253
xanthic, 326
Acids, nomenclature of, 113
polybasic, 135
Aconitine, 392
Acroleine, 400
Affinity, chemical, 158
how influenced, 160
Air-pumps, 24
Air-furnace, 136
Albite, 220
Albumen, 407
vegetable, 428
Aldehyde, 326
Alizarine, 397
Alcohol, 307, 444
Alkalimetry, 199
Alkarsin and alkargen, 334
Allantoin, 382
Alloxan, 382
Alloxantine, 385
Alumina, 218
sulphates, 218
silicates, 219
characters of salts of, 220
Aluminium, 218
chloride, 218
Alums, 219
Amalgamation-process, 263
Amalgams, 275
electrical, 78
Ammeline and ammelide, 380
Amidine, 300
Amidogen, 207
Ammonia, preparation and properties of, 140
compounds with anhydrous acids, 206
sulphate, 205
carbonate, 205
phosphates, 206
nitrate, 206
salts, characters of, 207
Ammoniacal amalgam, 204
Ammonium, 204
sulphurets, 206

Ammonium, chloride, 205
theory, 205
Amygdaline, 367
Amyle-compounds, 342
Analcine, 220
Analysis of water, 98
organic, 283, *et seq.*
of mineral water, 446, 448
Antiarine, 392
Antimony, 255
oxide, 255
sulphurets, 256
chloride, 255
characters of salts, 257
alloys of, 257
Aqua-regia, 123
Arabine, 302
Archil, 396
Argol, 308
Aricine, 391
Arrow-root, 301
Arsenic, 258
sulphurets, 259
Asphaltine, 437
Asphaltum, 437
Atmosphere, physical constitution of, 23
composition of, 103
Atmospheric pressure, 26
Atomic theory, 157
Atropine, 392
Augite, 217
Aurum musivum, 251
Axinite, 220
Azote, 102

B.

Balsams, 406
Barium, 208
oxides, 208
chloride, 208
sulphuret, 209
Baryta, 208
carbonate, 209
nitrate, 209
sulphate, 209
-salts, tests for, 209
Barometer, 27
chemical, 29
Batteries, voltaic, 80, and 162
Bay-salt, 204
Beer; brewing, 309
Benzamide, 349
Benzine, 347
Benzile, 350
Benzimide, 350
Benzoine, 349
Benzone, 347
Benzoyle-compounds, 345
Bezoar-stones, 421
Bile, composition of, 419
Binary theory of salts, 187
Bismuth, 240
oxides, 240
nitrates, 240
Bitumens, 437
Bleaching-powder, 213
Blood, composition of, 413
Blow-pipe, 137
Boiling-points of fluids, 42
Bones, composition of, 426
Boron, 131
Brain, composition of, 425
Brass, 244
Brazil-wood, 397
Bread, making of, 310
Breezes, land and sea, 66
Bromal, 324
Bromoform, 224, 341
Bromine, preparation and properties of, 128
Brucia, 391
Butter, 418
Butyrine, 402

C.

Cadmium, 239
compounds of, 240
Calculi, urinary, 424
biliary, 403
Calcium, 210, 439
protoxide, 210
peroxide, 211
chloride, 211
sulphurets of, 211
fluoride, 213
Calomel, 270
Caffeine, 393
Camphor, 404
artificial, 404
Cantharidine, 403
Caoutchouc, 406
Caramel, 296
Carbon, occurrence of in nature, 108, 439
crystalline forms of, 108
its compound with oxygen, 110
sulphuret of, 147
chlorides of, 322, 342

Carbonates, analysis of, 199
Carbonic oxide, preparation and properties of, 111
Carbyle, sulphate of, 323
Cassava, 301
Caseine, 409
  vegetable, 429
Catechin and catechu, 362
Cadriret, 438
Cements, 211
Cellulose, 302
  nitric, 305
Cerasine, 302
Cerine, 403
Cerium, 247
Chameleon mineral, 228
Charcoal, properties of, 109
Chemical philosophy, principles of, 148
Cheese, making of, 419
Chimneys, action of, 39
Chinoidine, 391
Chlorine, 120, 439
  preparation and properties of, 120
  compounds with oxygen, 124
Chloral, 324
Chloroform, 341
Chloro-cinnose, 354
Chlorosamide, 353
Chlorisatine, 396
Cholesterine, 403
Chondrine, 412
Chromium, 248
  oxide, 248
  sulphate, 248
  alum, 248
  chloride, 248
  characters of salts of, 249
Chrysen and pyren, 434
Chrysolite, 217
Chyle, 417
Cinchonia, 390
Cinnabar, 272
Cinnamyle-compounds, 253
Cinnameine, 355
Clays, composition of, 220
Coal-gas, 134
Coal-oil, 435
Cobalt, 237
  oxides, 237
  chloride, 237
  sulphate, 237
  oxalate, 237
  carbonate, 237
Cobalt, characters of salts of, 327
  ultramarine, 238
Cochineal, 397
Codeine, 389
Colchicine, 391
Colophony, 405
Coloring-principles, 394
Columbium, 254
Combination, laws of, 148
  by volumes, 153
Combining numbers, 151
  table of, 152
Combustion, 135
  at low temperatures, 97
Combustibility, relative, of gases, 139
Conduction of heat, 40
Condensation of gases, 50
Conicine, or conia, 391
Connecters, caoutchouc, 110
Copper, 242
  oxides, 243
  sulphate, 243
  nitrates, 243
  carbonates, 243
  chloride, 243
  arsenite, 243
  characters of salts of, 244
  alloys of, 244
Crystallization; crystallography, 177
Cryophorus, 52
Cudbear, 396
Curarine, 392
Cyanides, metallic, 369, *et seq.*
Cyanogen, 365
  chlorides of, 374
Cyanite, 220
Cystic oxide, 386, 425

D.

Daguerreotype, 62
Dammar-resin, 405
Daphnine, 392
Daturine, 392
Decomposition by electricity, 161
Delphinine, 392
Densities of bodies, 17
Density of vapors, determination of, 293
Dew, 66
Dew-point, 49
Dextrine, 300
Diamond, 108
Diastase, 301
  animal, 430
Diathermancy, 67

Diffusion of gases, 94
Dimorphism, 177
Displacement, collection of gases by, 94, 110
Distillation, 45
Dragon's blood, 405
Dutch-liquid, 321
Dyeing, principles of, 394

E.

Earthenware, manufacture of, 223
Ebullition, 42
Elaidine, 402
Elaterine, 392
Electricity, statical, 75
  voltaic, 80, 161
  animal, 82
  action of on the magnet, 82
  of steam, 85
Electro-chemistry, 161
Electrolysis, 162
Electrotype, 169
Electrophorus, 79
Elementary bodies, definition of, 87
Emetine, 392
Emulsine, 367
Enamel, 223
Equivalent numbers, 150, 439
  table of, 152
Erbium, 221
Erythroprotide, 411
Ethal, 403
Ether, 312
  continuous process for, 318
Ethers, compound, 312
Ether, heavy muriatic, 324
Etherole and etherine, 320
Eudiometer, Cavendish's, 99
  Ure's, 104
Eupione, 432
Evaporation at low temperatures, 47
Expansion of solids, 32
  fluids, 35
  gases, 37

F.

Fecula, 299
Felspar, 219
Fermentation, alcoholic, 307
  lactic, 310
  viscous, 311
Ferrocyanogen-compounds, 375
Ferridcyanogen-compounds, 377
Fibrine, 408
Fibrine, vegetable, 428
Flame, structure of, 135
Flames, hollow and solid, 96
Fluorine, 128
Fluor-spar, 213
Formulæ, deduction of, 292
Formomethylal, 341
Freezing of water by evaporation, 52
Fumaride, 361
Furnaces, principle of, 136
Fusel-oils, 345
Fustic-wood, 397

G.

Garnet, 220
Gas, illuminating, 134
Gases, liquefaction of, 50
Gas-holder, Pepys', 89
Gelatine, 411
Gentianine, 392
Gilding, 267, 268
Glass, manufacture of, 221
Gliadine, 428
Gluten, 428
Glucose, 297
Glucinum, 220
Glycerine, 401
Glycicoll, 412
Glycyrrhizine, 298
Gold, 266
  compounds of, 267
  alloys, 267
Goniometers, 177
Graphite, 108
Gravity, specific, 17
  specific, of gases, determination of, 92
Green, Scheele's, 243, 259
Guano, 387, 430
Gum, British, 301
  Arabic, 302
  tragacanth, 302
Gunpowder, 193

H.

Hatchetine, 438
Heat, conduction of, 40
  latent, 41
  capacity for, 53
  sources of, 55
  supposed central, 55
  developed by friction, 55
  radiation, reflexion, absorption, and transmission of, 64 *et seq.*

Hematoxyline, 397
Hematosine, 414
Hesperidine, 392
Heulandite, 220
Hornblende, 217
Hydrobenzamide, 349
Hydrogen, preparation and properties of, 93
peroxide of, 102
light carburetted, 132
sulphuretted, 142
persulphuret of, 143
phosphuretted, 144
seleniuretted, 144
arseniuretted, 259
Hydrometer, 22
tables, 441, 442
Hygrometer, Daniell's, 53
Hygrometry, 49
Hyoscyamine, 392

I.

Idrialine, 434, 438
Ilmenium, 171
Indigo, 394
Iodine, preparation and properties of, 126
chloride of, 147
Iodoform, 341
Inuline, 302
Iron, 228
oxides of, 229, 230
chlorides, 230
iodides, 230
sulphurets, 231
sulphates, 231
nitrate, 231
carbonate, 231
characters of salts of, 232
manufacure, 232
cast, varieties of, 233
Iridium, 277
Isatine, 396
Isomorphism, 184

J.

Jade, 217
Jet, 437
Jet, oxy-hydrogen, Daniell's, 96
Hemming's, 140

K.

Kalotype, 61
Kakodyle, and its compounds, 333
Kapnomor, 433
Katalysis, 161
Kelp, 126
Kermes-mineral, 256
Kreosote, 433
Kyanol, 435

L.

Lac, 405
Lamps, spirit, and gas, 138
safety, 139
Lantanum, 247
Laughing gas, 106
Laumonite, 220
Laws of combination, 148
Lead, 244
oxides, 245
nitrate, 245
carbonate, 245
action of water on, 246
chloride, 246
iodide, 246
characters of salts of, 246
alloys of, 247
Lead-tree, 170
Lecanorine, 396
Legumine, 429
Leucine, 411
Leukol, 435
Leyden jars, 79
Light, laws of, 56
reflexion, refraction, and polarization of, 56 *et seq*
decomposition of white, 59
chemical action of, 61
Lignine, 302
Lignite, 437
Lignone, 342
Lime, 210
sulphate, 211
carbonate, 212
phosphate, 212
chloride, 213
-salts, characters of, 215
Liquefaction of gases, 50
Liquor amnii, 418
Liquor of Libavius, 251
Litmus, 396
Lithium, 207
Loadstone, 230
Logwood, 397
Lupuline, 309
Lymph, 418

M.

Madder, 397

Magnesia, 215
sulphate, 216
carbonate, 216
alba, 216
phosphate, 216
estimation of, in analysis, 217
silicates, 217
characters of salts of, 217
Magnesium, preparation and properties of, 215
chloride of, 215
Magnetism, 71 *et seq.*
Magnets, artificial, 73
Magnetism of the earth, 73
Magneto-electricity, 84
Manganese, preparation and properties of, 225
oxides of, 225, 226
chloride, 227
sulphate, 227
carbonate, 227
characters of salts of, 228
Mannite, 299
Manures, action of, 430
Margarine, 399
Margarone, 400
Mariotte, law of, 27
Marsh's test for arsenic, 261
Mastic, 405
Meconine, 389
Meerschaum, 217
Melam and melamine, 379
Membranous tissue, 426
Mercaptan, 325
Mercury, 268
oxides of, 269
nitrates, 269
sulphates, 270
chlorides, 270, 271
iodides, 272
sulphurets, 272
characters of salts of, 273
Mysityle, 333
Mesotype, 220
Metacetone, 333
Metal, fusible, 241
gun, bell and speculum, 244
Metals, general properties of, 171
classification of, 188
Methyle-compounds, 337
Mica, 220
Milk, composition of, 418
Mineral pitch, 437
Mirrors, how silvered, 273
Molybdenum, 252
Moss, Iceland, starch from, 301
Carragheen, 301
Morphia, 388
Mortars, 211
Mucus, 418
Multipliers, 83
Murexan, 386
Murexide, 385

N.

Naphtha, 438
Naphthaline, 436
Narcotine, 389
Narceine, 389
Nervous substance, 425
Nickel, 235
oxides, 235
chloride, 236
sulphate, 236
carbonate, 236
characters of salts, 236
Nicotine, 391
Niobium, 171
Nitre, sweet spirits of, 314
Nitrobenzide, 348
Nitrogen, preparations and properties of, 102
its compounds with oxygen, 105
chloride of, 145
iodide of, 145
Nitrates, 106
Nitrous oxide, 106
Numbers, equivalent, 150, 439
Nutrition, function of, 427

O.

Oleine, 400
Olefiant gas, 133, 320
Oils and fats, 398
Oils, volatile, 403
Oils, palm and cocoa, 401
Oil of wine, heavy, 319
Oil of vitriol, preparation of, 114
Oil-gas, 134
Oil of turpentine, 404
lemons, 404
copaiba, 404
juniper, 404
storax, 404
roses, 404
peppermint, 404
cajeput, 404
mustard, 405

Oil of horseradish, 405
potatoes, 342
corn, 345
bitter-almonds, 345
cinnamon, 353
Opium, 388
Orcine, orceine, 396
Organic chemistry, 280
bodies, classification of, 281
decomposition of, by heat, 282
decomposition of, by decay and putrefaction, 282
analysis of, 283
Osmium, 279
Oxamethane 315
Oxamide, 304, 314
Oxides, classification of, 92, 174
Oxygen, preparation and properties of, 88
nomenclature of compounds, 92
Ozokerite, 438

P.

Palladium, 275
Palmitine, 401
Paraffine, 432
Paracyanogen, 365
Paramorphine, 389
Paranaphthaline, 436
Pectine, 302
Pelopium, 171
Petalite, 220
Petrolene, 437
Petroleum, 438
Pewter, 252
Philosophy, chemical, principles of, 148
Phloridzine, 353
Phosphorus, preparation and properties of, 117
compounds with oxygen, 118
chlorides of, 146
Phosgene gas, 112
Photography, 61
Picamar, 433
Picrotoxine, 392
Pile, voltaic, 80
Piperine, 392
Pit-coal, 437
Pittakal, 433
Platinum, 273
Platinum, spongy, 273
black, 274
oxides, 274
chlorides, 274
salts, combustible, 323
power of determining union of gases, 97
Plumbago, or graphite, 108
Pneumatic trough, 89
Polarization of light, 60
Polarity, magnetic, 72
Populine, 392
Porcelain, manufacture of, 223
Potassium, preparation and properties of, 190
peroxide of, 192
sulphurets of, 195
chloride, 196
iodide, 196
bromide, 197
Potash, 191
hydrate of, 191
carbonate, 192
bicarbonate, 192
nitrate, 193
sulphate, 194
bisulphate, 194
sesquisulphate, 194
chlorate, 194
hyperchlorate, 195
salts, test for, 197
Potato-oil and its compounds, 342
Precipitate, white, 271
Prehnite, 220
Pressure, correction for, 28
Proteine, 410
Protide, 411
Prussian blue, 376
Pseudomorphine, 389
Purple of Cassius, 252
Pus, 418
Pyrophorus, Homberg's, 219
Pyrometer, Daniell's, 34
Pyroxyline, 305

Q.

Quercitron bark, 397
Quicksilver, 268
Quina, 390

R.

Rays of the sun, chemical, 61
Reflexion, law of, 56
Refraction, law of, 57
indices of, 58

Resins, 405
Respiration, 416
Retinite, 438
Reverberatory furnace, 136
Rhodium, 276
Ropiness of wines, &c., 302
Ruthenium, 171

S.

Safety-jet, Hemming's, 140
Safety-tube for distillatory-vessels, 123
Saffron, 397
Sago, 301
Salep, 301
Salicine, 351
Salicyle-compounds, 351
Sal-alembroth, 271
Salts, theory of, 174, 187
    sulphur, 176
    binary theory of, 187
Selenium, 117
Serpentine, 217
Silicon, 129
Siliceous minerals, analysis of, 130
Silver, 263
    oxides, 264
    nitrate, 265
    sulphate, 265
    hyposulphite, 265
    chloride, 265
    iodide, 265
    sulphuret, 266
    ammoniuret, 266
    characters of salts of, 266
    alloy of, 266
    German, 236
Skin, 426
Smalt, 237
Soaps, saponification, 399
Sodium, preparation and properties of, 197
    sulphuret of, 203
    chloride, 203
    iodide and bromide, 204
Soda, hydrate of, 197
    carbonate, 198
    bicarbonate, 199
    sulphate, 201
    bisulphate, 202
    hyposulphite, 202
    nitrate, 202
    phosphates of, 202
    biborate, 203
Solanine, 392
Solder, 247
Specific heat, 53
    gravity, 17
        of airs, 92
Spectrum, solar, 58
Speiss, 235, 238
Spermaceti, 403
Spiræa ulmaria, oil of, 351
Spirit, proof, 308
Spodumene, 220
Starch, 299
    from Iceland moss, 301
        Carragheen moss, 301
Steam, elastic force of, 44
    baths, 44
    engine, 45
Stearine, 399
Steatite, 217
Steel, 234
Stilbite, 220
Stoneware, manufacture of, 223
Stramonine, 392
Strontium, 210
    peroxide, 210
    chloride, 210
Strontia, 210
    nitrate, 210
Strychnia, 391
Sublimate, corrosive, 271
Sugar, cane, 295
    grape, 297
    action of acids on, 297
        alkalis on, 298
    eucalyptus, 298
    from ergot of rye, 298
    of diabetes insipidus, 298
    of liquorice, 298
    of milk, 299
    manna, 299
Sulphur, occurrence in nature, 112
    properties of, 112
    compounds with oxygen, 113
    chloride of, 146
Sulphuretted hydrogen, 142
Sulphocyanogen-compounds, 378
Sulphobenzide, 348
Symbols, table of, 155
Systems, crystallographical, 180
Synaptase, 367

T.

Tapioca, 301
Tar, varieties of, 432
Taurine, 420
Teeth, 427
Tellurium, 257

Test-acid for alkalimetry, 199
Terbium, 221
Thermometer, construction of, 31
    scales, 31
Theine, 393
Thebaine, 38
Theory, atomic, 157
Theobromine, 393
Thorium, 221
Tin, 250
    oxides, 250
    chlorides, 251
    sulphurets, 251
    characters of salts of, 251, 252
Tinned-plate, 252
Titanium, 254
Trade-winds, 39
Tungsten, 252
Turmeric, 397
Type-metal, 257

U.

Uramile, 384
Uranium, 241
Urea, 372, 380.
Urethane, 316
Urine, composition of, 421
Urinary calculi, 424
Ulmine, 298
Ultramarine, 203

V.

Vapor, aqueous, specific gravity of, 48
    elastic force of, 44, 443
Vapors, density of, 48
    hypothetical density of, 154
Vaporization at low temperatures, laws of, 47
Vanadium, 253
Varvicite, 227
Vegeto-alkalis, 388
Ventilation, 39
Veratria, 391
Verdigris, 331
Vermilion, 272
Vinegar, 329
Vitriol, white, 238
    blue, 243
    green, 231
Volatile oils, 403
Volumes, combination by, 153
Voltameter, 165

W.

Water, composition of, 98
    of crystallization, 176
    properties of, in a pure state, 100
    of sea and mineral springs, 100, 446, 448
    compounds of, 101
    basic powers of, 176
Wax, 403
Weights and measures, 445
Wire-drawing, 172
Wines, 308
Wood-spirit and its compounds, 337
    ether, 338
Woody fibre, 302

X.

Xanthic oxide, 386, 425
Xyloidine, 305
Xylite, 342

Y.

Yttrium, 221

Z.

Zinc, 238, 440
    oxide of, 238
    sulphate, 238
    carbonate, 239
    chloride, 239
    characters of salts of, 239
Zirconium, 221

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